SUSTAINABLE UTILISATION OF RAW SEWAGE SLUDGE (RSS) AS A WATER REPLACEMENT IN CEMENT-BASED MATERIALS CONTAINING UNPROCESSED FLY ASH

Alaa A Hamood

A thesis submitted in partial fulfilment of the requirements of the University of Wolverhampton for the degree of Doctor of Philosophy

August 2014

This work or any part thereof has not previously been presented in any form to the University or to any other body whether for the purposes of assessment, publication or for any other purpose (unless otherwise indicated). Save for any express acknowledgements, references and/or bibliographies cited in the work, I confirm that the intellectual content of the work is the result of my own efforts and of no other person.

Signature ……………Alaa Hamood…………………………..

Date …………………05/08/2014………………………………

ABSTRACT

Prior to the implementation of the European Union Urban Waste Water Treatment Directive (91/271/EEC) in 31 Dec 1998, around a quarter of the sewage sludge produced in the UK was either discharged to surface waters via pipes or disposed from ships at sea. Discontinuing this route together with the quality requirements of the European Waste Water Directive, led to the generation of significant quantities of sewage sludge. It has therefore become required to treat this waste effectively before it can be sent back to the environment. Consequently, this added greater challenges for the environmental agencies, as well as local authorities. The treatment process comprises costly and energy consuming applications including physical, chemical, biological and thermal. In addition to the sewage sludge, the power generation industry produces massive quantities of fly ash from burning coal. In the UK, there is about 5,300,000 tonnes of fly ash that are generated annually, which require to be processed and classified in order to meet the standard requirements before it can be used in the construction applications. The classifying process also involves a series of costly and energy consuming mechanical and physical applications.

This research programme has introduced an innovative alternative to the traditional re-use and disposal routes of Raw Sewage Sludge (RSS) and unprocessed fly ash. It has suggested the utilisation of RSS and unprocessed fly ash as raw ingredients for the production of sustainable construction materials. This research programme has therefore examined the performance of cement-based materials containing Raw Sewage Sludge (RSS) as a water replacement and unprocessed fly ash as cement replacement. Mortar and concrete mixes incorporating these materials were tested for their flowability/workability, density, Total Water Absorption (TWA), Ultrasonic Pulse Velocity (UPV), compressive strength, flexural strength, drying shrinkage, sulphate attack and leaching properties. Three series of cement-based materials were studied including mortar mixes with RSS and unprocessed fly ash (Series 1), mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2), and concrete mixes with RSS and unprocessed fly ash (Series 3).

The outcomes of the investigation were encouraging in that cement-based materials containing RSS and unprocessed fly ash that were produced demonstrated relatively good engineering, durability and environmental properties in comparison to the control mixes. The inclusion of unprocessed fly ash significantly reduced flowability/workability; however it improved long-term compressive strength for both mixes with RSS and water. The best compressive strength results were recorded when cement was replaced with 10-20% unprocessed fly ash by weight of total binder. The results also showed that sulphate attack resistance improved when fly ash was included. Moreover, safe concentration levels of heavy metals and free ions were detected when leaching test was performed. However, it must be kept in mind that more environmental tests must be performed before any large scale use is undertaken.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGEMENTS

I would like to express my sincere gratefulness to the Director of Studies, Professor Jamal Khatib, for his help, advice, encouragement, patience and continuous support throughout the preparation of this work.

I would like to thank Professor Craig Williams for his expertise and guidance with regards to the environmental aspect of this work.

I would like to acknowledge the support of the technical staff in the construction and environmental laboratories, Mr Geoffrey Cooper, Mr Raymond Bradley, Mrs Diane Spencer, Mr David Townrow, Mrs Barbara Hodson and Miss Charlene Butler.

I would like to thank all the members of staff at University of Wolverhampton, especially Professor Bob Newman, Mr Chris Williams, Dr Paul Lister, Dr Jessica Lamond, Professor Sabah Mushatat, Dr Ezekiel Chinyio, Dr David Searle, Mr Peter Mills, and Mrs Riz Shah.

I would also like to thank my former tutor, Dr Nicholas Hytiris from Glasgow Caledonian University, for his contributions towards the initial research proposal.

I would like to give my sincere appreciation to my family and friends for their support and encouragement throughout my research at the personal level, in particular, my beloved wife & her family, my brothers, my sisters, and my extended family.

To all of the rest who made a difference…..Thanks

DEDICATION

This thesis is dedicated to my parents, for their endless love, support and encouragement.

This thesis is dedicated to the memory of my late uncle, Hadi Hamood

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

Raw Sewage Sludge is a residual stream of suspended/dissolved organic and inorganic materials that result from the treatment processes of municipal wastewaters. Raw Sewage Sludge is usually in the form of liquid or semisolid liquid that typically contains, depending on operation and processes applied, from 2 to 8 percentage solids by weight (Metcalf & Eddy et al., 2003). In wastewater treatment plants, Raw Sewage Sludge is mainly collected from primary settlement tanks, which are large round or rectangular tanks where heavier particles are allowed to settle to the bottom and to be later swept by scrapers to a submerged outlet. Settled stream is pumped, in the form of thick slurry, to the sludge storage and treatment unit for further processing. Raw Sewage Sludge may also be collected from secondary and tertiary settlement tanks.

At sewage sludge storage and treatment units, further biological, chemical and physical processes are applied to reduce water content and to eliminate potential associated hazards. Hazards include high heavy metal contents, presence of dangerous pathogens and risks associated with the biodegradation of organic matters (production of flammable gases and unpleasant odours). Treatment processes include preliminary operations, thickening, stabilisation, conditioning, dewatering, heat drying and other processing and thermal reduction.

There are approximately 35 million tonnes of Raw Sewage Sludge produced in the UK each year. These quantities are reduced to 25 million tonnes per year by applying further on site physical and chemical processes (Waste on line, 2010). In 2010, 1.41 million tonnes of dry solids were produced from sewage sludge in England and Wales (Defra, 2012).

Prior to the implementation of the European Union Urban Waste Water Treatment Directive (91/271/EEC) in 31 Dec 1998, around a quarter of sewage sludge produced in the UK was either discharged to surface waters via pipes or disposed from ships at sea (Defra, 2012). The cease of this route together with the higher standards required by the European Waste Water Directive, generate significant quantities of sewage sludge adding greater challenges for both environmental agencies as well as local authorities. Since then, the traditional re-use and disposal ways have had to be replaced by effective alternatives to improve waste management practices currently in place, and to meet the Directive deadlines. Alternatives include the utilisation of sewage sludge products in the construction industry for the production of sustainable construction materials.

In addition to the significant amounts of Raw Sewage Sludge produced in the UK, the power industry generates significant quantities of fly ash from burning coal. In the UK, there is about 5,300,000 tonnes of fly ash are produced annually (Sear, 2011). Unprocessed fly ash is not suitable for use in the construction applications due to its high carbon content and large particle size. Unprocessed fly ash therefore is required to be treated and classified to meet the requirements of the European Standards. The classifying process involves a series of costly and energy consuming mechanical and physical applications.

1.2 NOVELTY AND SIGNIFICANCE OF THE RESEARCH

This experimental work presented an innovative alternative to the traditional methods of treating and re-using Raw Sewage Sludge (RSS) and unprocessed fly ash. Due to the fact that it contains about 97% water of total mass, Raw Sewage Sludge (RSS) was suggested to be used as a water replacement in cement-based materials. In addition and despite that there is very limited information about the utilisation of unprocessed fly ashes in the construction applications, the literature suggested that the incorporation of this material would positively contribute to the mechanical and durability properties. Therefore, unprocessed fly ash was also incorporated in this experimental programme as cement replacement in mortar and concrete mixes containing RSS.

In addition to the production of sustainable construction materials, the outcome of this research could see huge financial savings to the current economical constraints by eliminating the costly processes involved in treating these wastes. This would also lead to a huge reduction in energy consumption. Furthermore, there are huge environmental benefits from the prevention of RSS transportation to landfills and incinerators.

1.3 AIMS AND OBJECTIVES

The general aim of this research is to examine and investigate the performance of cement-based materials containing Raw Sewage Sludge (RSS) as a water replacement and unprocessed fly ash as cement replacement. The performance included the fresh, engineering, durability and environment properties of mortar and concrete mixes incorporating these materials. This aim was achieved through the following objectives:

1. To examine the flowability/workability of cement-based materials containing RSS and unprocessed fly ash.
2. To evaluate the physical properties, including density and Total Water Absorption (TWA), of cement-based materials containing RSS and unprocessed fly ash.

3. To determine the mechanical properties, including Ultrasonic Pulse Velocity (UPV), compressive strength, length change and flexural strength, of cement-based materials above
4. To assess the sulphates resistance of mortar and concrete mixes containing RSS and unprocessed fly ash.
5. To evaluate the leaching properties of mortar mixes incorporating RSS and unprocessed fly ash.
6. To examine the relationship between different properties including compressive strength with density, compressive strength with TWA, compressive strength with UPV, and compressive strength with flexural strength.
7. To predict the compressive strength with age using one more variable including RSS content, sand content or fly ash replacement.

1.4 EXPERIMENTAL PROGRAMME

Figure 1.1 shows the experimental programme that was carried out to achieve the objectives of this research (also refer to Tables 3.7, 3.8, 3.9 and 3.10). The experimental work consisted of three series of cement-based materials containing RSS and unprocessed fly ash.

Series 1 consisted of 17 different mixes that were divided into 5 groups. Each group had one variable consisting of either RSS content, sand content or fly ash content. This series was tested for various properties including flowability, density, Total Water Absorption (TWA), Ultrasonic Pulse Velocity (UPV), compressive strength, flexural strength, length change, sulphate resistance and leaching test. A brief summary about each group in this series is as follows:

- Group 1: the main objective of this group was to investigate the influence of varying RSS content on the above properties. One sand to cement ratio of 4.5 and four RSS/Cement ratios of 0.5, 0.65, 0.8 & 1 were used.
- Group 2: this group was designed to assess the impact of varying sand content on the above properties. One RSS/Cement ratio of 0.8, and four sand to cement ratios of 3, 4.5, 6 and 7.5 were used.
- Group 3: this group was designed to evaluate the impact of partially replacing cement with unprocessed fly ash on tested properties. Four unprocessed fly ash replacements of 0, 10, 20 and 30% by weight of total binder, and one RSS/Binder ratio of 0.65 were considered. One sand to cement ratio of 4.5 was used.
- Group 4: similar to group 3, but with a higher RSS/Binder ratio (0.8).

- Group 5: the composition of this group was similar to Group 4, but using water. This group was considered as the control and the results were compared with Group 4.

Series 2 consisted of four mortar mixes that contained RSS with large proportions of unprocessed fly ash, and one mortar mix made with water. Series 3 comprised four concrete mixes that incorporated RSS and unprocessed fly ash. One more concrete mix that made with water was also examined.

Variables	Series 1					Series 2	Series 3
	Group 1	Group 2	Group 3	Group 4	Group 5	Mixes with large proportion of fly ash	Concrete mixes
Mix number	M1, M2, M3 & M4	M5, M3, M6 & M7	M2, M11, M12 & M13	M3, M8, M9 & M10	M14, M5, M16 & M17	MLRef, ML1, ML2, ML3 & ML4	CMRef, CM1, CM2, CM3 & CM4
Liquid/Binder	0.5, 0.65, 0.8 & 1	0.8	0.65	0.8	0.8	1	0.5
Sand:Cement	4.5	3, 4.5, 6 & 7.5	4.5	4.5	4.5	4.5	1:1.5:3 (C:S:G)
Fly ash %	0	0	0, 10, 20 & 30	0, 10, 20 & 30	0, 10, 20 & 30	0, 40, 60 & 80	0, 10, 15 & 20
Liquid type	RSS	RSS	RSS	RSS	Water	RSS & Water	RSS & Water

Property	Series 1					Series 2	Series 3
	Age(days)					Age(days)	Age(days)
	1 | 7 | 28 | 90 | 365	1 | 7 | 28 | 90 | 365	1 | 7 | 28 | 90 | 365	1 | 7 | 28 | 90 | 365	1 | 7 | 28 | 90 | 365	1 | 7 | 28 | 90 | 180	1 | 7 | 28 | 90 | 300
Density	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓
TWA	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓
UPV	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓
Compressive Str.	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓	✓ ✓ ✓ ✓ ✓
Drying shrinkage	✓	×	✓	✓	✓	×	✓
Flexural Strength	× ✓ ✓ ✓ ✓	× × × × ×	× ✓ ✓ ✓ ✓	× ✓ ✓ ✓ ✓	× ✓ ✓ ✓ ✓	× × × × ×	× × ✓ × ×
Sulphate attack	✓	✓	✓	✓	✓	×	×
Leaching Test	✓	✓	✓	✓	✓	×	✓

Figure 1.1: Experimental programme.

1.5 SCOPE OF THE PRESENT INVESTIGATION

The current thesis has been divided into nine chapters, whose structure and content are presented in Figure 1.2.

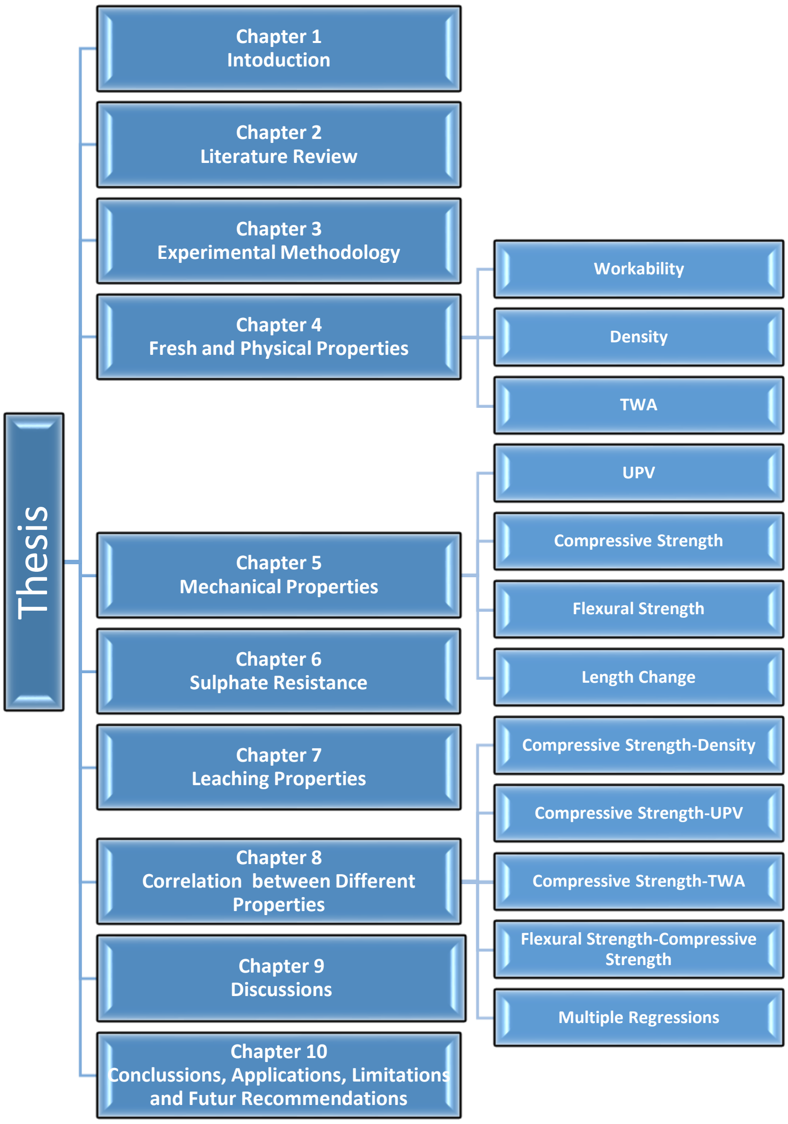


Figure 1.2: Structure and content of the thesis.

This chapter, **Chapter 1: "Introduction"** provides an overview about the research topic including the aims, objectives and the experimental plan of the research work. It also provides a brief summary of the content of each chapter.

Chapter 2: "Literature Review" gives detailed information about sewage sludge, including sewage sludge properties, production and treatment. It also provides a detailed review of the recent research in utilising sewage sludge products in the construction industry, and summarises the key findings. Review includes the use of sewage sludge products in ceramic and ceramic tiles manufacturing, incinerated sewage sludge ash in cement-based materials, sewage sludge in lightweight construction materials, soil stabilisation using sewage sludge, civil engineering applications and finally sewage sludge in mortar and concrete mixes.

In addition, this chapter provides detailed information about fly ash including fly ash properties, production and utilisation. It also discusses the influence of incorporating fly ash in cement-based materials on fresh, hardened and durability properties. Properties include setting time, workability and bleeding, temperature rise, density, length change, ultrasound pulse velocity (UPV), strength development and sulphate resistance.

This chapter also covers additional areas including the chemical reaction and hydration process of cement products, sulphate attack mechanism and chemical changes, and the use of rejected and unprocessed fly ash in the cement-based systems.

Chapter 3: "Experimental Methodology" provides detailed description of materials, instruments and techniques used throughout the experimental programme. The chapter also gives detailed information about the composition of tested mixes, as well as materials preparation, sample casting, curing, and testing ages. Additional information about the instruments and machinery used to perform different tests is also included. Finally, the chapter briefly describes instruments used to perform the analytical tests for unprocessed fly ash and RSS samples, as well as, the instruments used to perform the leaching tests.

Chapter 4: "Fresh and Physical Properties" evaluates the fresh and physical properties of three series of cement-based materials including mortar mixes with RSS and unprocessed fly ash (Series 1), mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2), and concrete mixes with RSS and unprocessed fly ash (Series 3). The properties include flowability/workability, density and Total Water Absorption (TWA).

The flowability of mortar mixes was obtained in accordance to BS EN 1015-3:1999 (BSI, 1999a), whereas the workability of the concrete mixes was obtained using BS EN 12350-2:2009 (BSI, 2009a). The density for the mortar mixes was determined manually by recording both weight and dimensions. The density of the concrete mixes was obtained in compliance with the requirements of BS EN 12390-7:2009 (BSI, 2009d). For the determination of the TWA, cured specimens were dried in an electrical oven at 75°C until a constant weight. Thereafter, dried specimens were cooled at room temperature and their mass was measured. Dried samples were immersed in water until a constant mass (for up to 10 days), and mass of the saturated samples was taken. Total water absorption was calculated using Formula 3.4, and was recorded to the nearest 0.01%.

Chapter 5: "Mechanical Properties" assesses the mechanical properties including Ultrasonic Pulse Velocity (UPV), compressive strength, flexural strength and drying shrinkage of all three series. The UPV was obtained using Proceq Pundit Lab+ instrument (refer to section 3.6.7). The compressive strength of mortar mixes was determined in accordance to ASTM C109/C109M-02 (ASTM, 2008) using SERCOMP7 hydraulic compressive strength machine with a loading rate of 2400 N/sec. The compressive strength of concrete specimens were obtained following test procedures described in BS EN 12390-3:2009 (BSI, 2009b), with loading rate of 0.6 MPa/sec. The flexural strength of the mortar mixes was obtained in compliance with the requirement of BS EN 1015-11:1999 (BSI, 1999b), whereas BS EN 12390-5:2009 (BSI, 2009c) was followed for the concrete samples. For the determination of length change due to drying shrinkage, two pairs of demec-studs were attached, at a distance of 100mm from each other, to the two sides of prism that have been cast against the steel mould. 40x40x160 mm in size prism was used for mortar mixes and 75x75x280 mm in size for concrete mixes. A digital gauge was used on a frequent time intervals to monitor length change.

Chapter 6: "Sulphate Resistance" evaluates the performance of cement-based materials subjected to sulphate attack. Samples from both Series 1 and Series 3 were cured for 28 days, and were later fully immersed in 5% (by weight) sulphate solution. Sulphate attack was evaluated by measuring change in weight, compressive strength and visual observation during approximately 365 days of continues exposure to sulphate attack.

Chapter 7: "Leaching Properties" reports the concentration of detected pollutants presented in eluates (leaching sample) of mortar mixes containing RSS and/or unprocessed fly ash. Pollutants include heavy metals (Al, Fe, Co, Ni, Cu, Zn, Mn, Cd, Ba, Se, As, Mo, Cr, Pb and Sn) and free ions (Bromide, Chloride, Fluoride, Nitrite, Nitrate, Phosphate and Sulphate). The volume of water that was required to immerse test specimens (the leachant) and time intervals for the eluates (leaching sample) to be collected were determined in accordance to Draft BS EN 15863 (BSI, 2008d). Collected eluates were analysed using Ion Chromatography System (ICS) and Inductively Coupled Plasma (ICP).

Chapter 8: "Correlation between Different Properties" investigates the correlation between different physical and mechanical properties of cement-based materials incorporating RSS and unprocessed fly ash. In particular, this chapter discusses the relationship between compressive strength and various properties including, Ultrasonic Pulse Velocity (UPV), Total Water Absorption (TWA), and flexural strength. It also discusses the multiple regressions of compressive strength with curing age and one additional parameter including RSS content, fly ash content and sand content. It also suggests numerical functions to relate the different properties.

Chapter 9: “Discussions” discusses the results of tested properties and their correlation that are reported in Chapters 4, 5, 6, 7 and 8. The tested properties include fresh & physical properties, mechanical properties, sulphate resistance (sulphate attack), and environmental properties (leaching test).

Chapter 10: “Conclusions, Applications, Limitations and Future Recommendations” states the main conclusions and defines the limitations. It also suggests future recommendations with regards to the utilisation of both RSS and unprocessed fly ash for the construction applications.

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

Recent environmental and engineering research focus on the application of sustainability and sustainable environment to improve waste management practices in place, and to reduce high energy levels that are currently consumed in waste treatment. A number of international studies were therefore undertaken to investigate the possibility of obtaining effective alternatives to the traditional ways of treating and disposing waste. Alternatives comprise utilising waste products in the construction industry for the production of sustainable construction materials.

Prior to the implementation of the European Union Urban Waste Water Treatment Directive (91/271/EEC) in 31 Dec 1998, around a quarter of sewage sludge produced in the UK was either discharged to surface waters via pipes or disposed from ships at sea (Defra, 2012). Discontinuing this route together with the higher standards required by the European Waste Water Directive, generated significant quantities of sewage sludge. This added greater challenges for both environmental agencies and local authorities. Since then, the traditional re-use and disposal ways have had to be replaced by effective alternatives to improve waste management practices currently in place, and to meet the Directive's deadlines. Alternatives include the utilisation of sewage sludge products in the construction industry for the production of sustainable construction materials.

In addition to the significant amounts of Raw Sewage Sludge produced in the UK, the power generation industry produces massive quantities of fly ash from burning coal. Unprocessed fly ash is not permitted for use in the construction applications due to its high carbon content and large particle size (Poon et al., 2003). Unprocessed fly ash therefore required to be fully treated and classified to meet the requirements of the European Standards. The classifying process involves a series of costly and energy consuming mechanical and physical applications.

2.2 SEWAGE SLUDGE

2.2.1 Scope

This section provides detailed information about sewage sludge. This includes sewage sludge properties, production and treatment. It also provides a detailed review of the recent research in utilising sewage sludge products in the construction industry, and summarises the key findings. Review includes the following areas:

- Sewage sludge products in ceramic and ceramic tiles manufacturing
- Lightweight construction materials
- Soil stabilisation
- Civil engineering applications
- Sewage sludge products in cement-based systems

2.2.2 Raw Sewage Sludge

Raw Sewage Sludge is a residual stream of suspended/dissolved organic and inorganic materials that results from the treatment processes of municipal wastewaters. Raw Sewage Sludge is usually in the form of liquid or semi-solid liquid that typically contains, depending on operation and processes applied, from 2 to 8 present solids by weight (Metcalf & Eddy et al., 2003). In wastewater treatment plants, Raw Sewage Sludge is mainly collected from primary settlement tanks, which are large round or rectangular tanks where heavier particles are allowed to settle to the bottom and to be later swept by scrapers to a submerged outlet. Settled stream is pumped, in the form of thick slurry, to the sludge storage and treatment unit for further processing. Raw Sewage Sludge may also be collected from secondary and tertiary settlement tanks. Figure 2.1 shows the typical wastewater treatment processes.

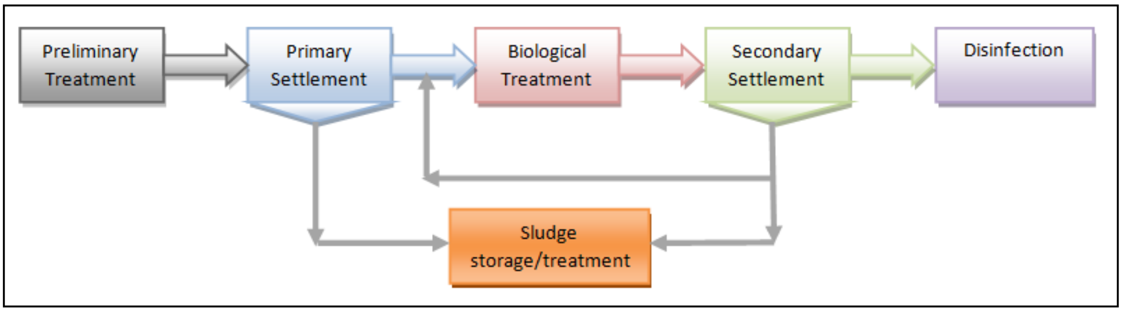


Figure 2.1: Typical wastewater treatment processes-adopted from (Metcalf & Eddy et al., 2003).

Properties of Raw Sewage Sludge are varying depending mainly on collection seasons, as well as, on applied treatment processes to source wastewater. Table 2.1 shows the typical chemical composition and properties of Raw Sewage Sludge.

Table 2.1: Typical chemical composition and properties of Raw Sewage Sludge (Metcalf & Eddy et al., 2003).

Item	Range	Typical
Total dry solids (TS) %	2-8	5
Volatile solids (% of TS)	60-80	65
Grease and fats (% of TS)	6-35	-
Protein (%of TS)	20-30	25
Nitrogen (N, % of TS)	1.5-4	2.5
Phosphorus (P_2Of, % of TS)	0.8-2.8	1.6
Potash (K_2S, % of TS)	0-1	0.4
Cellulose (% of TS)	8-15	10
Iron (not as sulphide)	2-4	2.5
Silica (SiO_2,% of TS)	15-20	-
PH	5-8	6
Alkalinity (mg/L as $CaCo_3$)	500-1500	600
Organic acids (mg/L as HAc)	200-2000	500

2.2.3 Raw Sewage Sludge treatment

At sewage sludge storage and treatment units, further biological, chemical and physical processes are applied to reduce water content and to eliminate potential associated hazards. Hazards include high heavy metal contents, presence of dangerous pathogens and risks associated with the biodegradation of organic matters (production of flammable gases and unpleasant odours). Treatment processes include preliminary operations, thickening, stabilisation, conditioning, dewatering, heat drying & other processing and thermal reduction. Figure 2.2 shows the general sewage sludge treatment procedures.

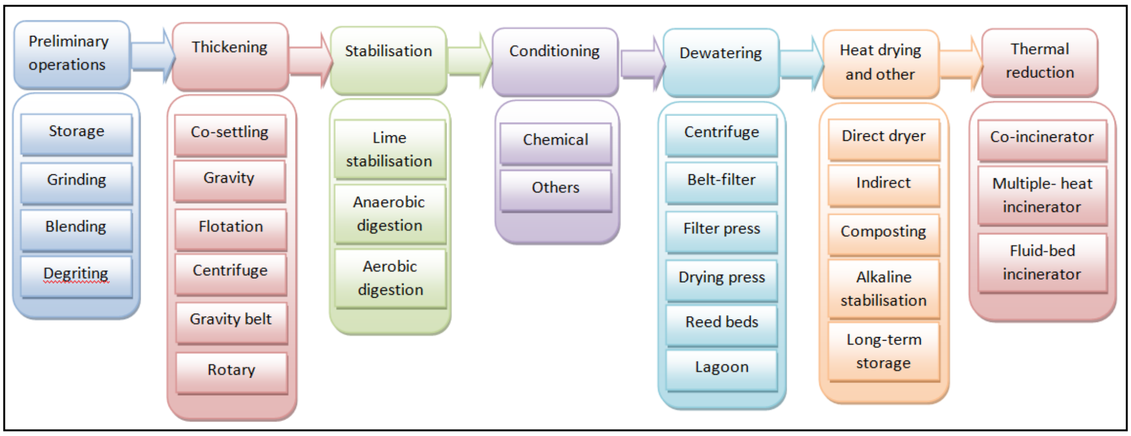


Figure 2.2: Generalised sludge-processing flow diagram –adopted from (Metcalf & Eddy et al., 2003).

Following procedures showed in Figure 2.2, Raw Sewage Sludge can be treated partially or fully depending on the quality of the final product. Treatment level also depends on many other factors including on site treatment facilities, associated cost, energy consumption and in-place environmental regulations. Different sewage sludge products have different biological and physical properties, subject to the level and type of applied treatment. Properties include consistency, texture, colour, odour strength, biological activity and water content (Table 2.2).

Table 2.2: Sewage sludge forms/treatment and properties.

Terminology and Treatment level	Colour/odour	Consistency	Moisture content % of total weight	Reference
Raw Sewage Sludge, Crude Sewage Sludge, Primary Sewage Sludge or Untreated Sewage Sludge	Grey with extremely offensive odour	Thick liquid/slurry	92-98	(Metcalf & Eddy et al., 2003)
Dewatered Sewage Sludge, Sludge Cake or Wet Sewage Sludge	Dark grey with faint odour	Thick past	50-85	
Dried Sewage Sludge, Thermally Dried Sewage Sludge, Dehydrated Sewage Sludge or Composted Sewage Sludge	Dark grey inert material	Dried pellets	5-10	(Wang et al., 2009)
Incinerated Sewage Sludge Ash (ISSA)	Dark inert material	Powder	0	(Monzó et al., 1999)

2.2.4 Sewage sludge production and management

There are approximately 35 million tonnes of Raw Sewage Sludge produced in the UK each year. These quantities are reduced to 25 million tonnes per year by applying further on site physical and chemical processes (Waste on line, 2010). In 2010, 1.41 million tons of dry solids were produced from sewage sludge in England and Wales (Defra, 2012).

Sewage sludge is wildly used in agriculture as fertilizers and soil conditioner for being rich in nutrients, trace elements and organic matter. It improves soil conditions, saves the energy required for the production of industrial fertilisers and recycles phosphorus. Sewage sludge can also be used in land reclamation and can be used as fuel in two ways; using dried sludge pellets as a fossil fuel replacement or by burning biogases, produced from digestion process, in engines to generate electricity. Table 2.3 shows the reuse and recycling routes for sewage sludge in England and Wales in three different years.

Table 2.3: Sewage Sludge management in England and Wales in tonnes dry solids (Defra, 2012).

Reuse or disposal route	Sludge Discharge to surface water			Sludge Reuse		Sludge Disposed			Total
	Pipelines	Ships	Others	Soil & Agriculture	Others	Landfill	Incineration	Others	
1992	8,430	273,158	-	440,137	32,10	129,748	89,8000	24,300	997,673
2008	-	-	-	1,241,639	90,845	10,882	185,890	1,523	1,530,779
2010	-	-	-	1,118,159	23,385	8,787	259,642	2,863	1,412,836

2.2.5 Sewage sludge products in the construction and civil engineering applications

2.2.5.1 In ceramic and ceramic tiles manufacturing

Ceramics are inorganic inert materials made of sintering raw earth resources (clay, quartz, feldspar, stoneware and porcelain, which is often made from kaolin) at a temperature of 1000^{o}C and above to produce durable and stiff materials that can be used for engineering and other applications. Engineering applications include the manufacturing of ceramic tiles, clay brick and lightweight aggregate.

Jordan et al. (2005) prepared ceramic tile body samples (5X5cm) made of standard ceramic clay mixed with different proportions of dry composted sewage sludge (0-10 % of total weight). Samples were prepared using uniaxial pressing. Samples were later dried in stove and heated in an electric kiln following a standard heating cycle for high porosity ceramic. Samples were tested for their bending resistance and water absorption. Results showed that the increase of sludge ratio would increase water absorption and would decrease bending strength.

Favoni et al. (2005) investigated the possibility of fully replacing traditional ceramic clay with powder mixes containing thermally dried sewage sludge and steelworks slag. Cylindrical (0.6x50 mm) or rectangular (4x5x50 mm) samples were pressed and sintered in electric muffle at 1050-1150^{o}C. Results showed an appropriate level of immobilising hazardous substances contained in the original powders, and a fairly good mechanical strength compared to traditional ceramics. These materials can be used for the production of monolithic ceramic bodies where colours are not important for the final product finish.

Montero et al. (2009) conducted a research to study the impact of adding dry composted sewage sludge and marble residues (0-10% sewage sludge and 0-35% marble residue) to standard clay used in manufacturing ceramic tile bodies. Results showed that this would provide a better sintering of original powders, and this was due to the improvement of reactivity between used substitutes and clay menials and quartz. However, the technical properties of the final ceramic products, incorporating sewage sludge and marble residues, showed an increase in water absorption and decrease in bending resistance, and therefore the total amount of added waste material must be controlled to produce the ceramic tiles to the required quality.

Qi et al. (2010) studied the possibility of using Dehydrated Sewage Sludge (DSS) pellets, which were produced by thermally treating sewage sludge, as a clay replacement for the production of Ultra-Lightweight Ceramics (ULWC) products. ULWC were prepared under optimum conditions (addition of DSS was 30%, preheated at 400^{o}C for 20 min and sintered at 1150^{o}C for 10 min). Results showed that samples incorporated DSS pellets gave low bulk density, good waterproof properties and safe environmental properties when leaching test was performed.

Cusidó and Soriano (2011) used sewage sludge pellets, which are normally produced by drying sewage sludge in low temperature rotatory kilns, as an alternative material for the natural clay to produce light weight construction ceramics. Pellets were fired in a furnace at up to 1050^{o}C and then tested for engineering and environmental properties. Results showed that ceramics made of sewage sludge pellets have a low thermal conductivity, undetectable amount of hazardous materials when leaching test was performed, and no toxic emissions were detected during the firing process.

Park et al. (2002) prepared glass and glass ceramics specimens made of incinerated sewage sludge fly ash, with and without 10% of CaO (by weight). Prepared samples were heated at 760^{o}C for 1 hour, and then fired at a region of 1050-1200^{o}C. The addition of CaO decreases the melting temperature, which provides further economic benefits. Glass-ceramics fired at 1050^{o}C for 2 h showed a microhardness of 6230 MPa and a bending strength of 92 MPa. Glass-ceramics containing large amounts of diopside (1050^{o}C/2 hours) generally showed better physical and chemical properties than their anorthite counterparts due to the interlocking microstructures of diopside crystals.

Merino et al. (2007) tested high probes ceramics samples (46mm height and 23mm inner diameter) made of incinerated sewage sludge ashes, clayey additives (kaolin, montmorillonite, and illitic clay) and powdered flat glass. Samples were subjected to a firing temperature of 1000-1200^{o}C. Specimens were then tested for their engineering properties, including water absorption and compressive strength. Results showed that ceramic construction materials could be obtained by firing sewage sludge ashes only. However, using the additives stated above improved some engineering properties such as compressive strength.

Mixing Incinerated Sewage Sludge Ash (ISSA) in different proportions with pottery and porcelain clay for the production of tiles, was investigated by Chen and Lin (2009b). Nano-SiO_2 was added to the mixes to improve engineering properties by expelling excess air. They were pressed by a machine with a vertical pressure of 35 ± 0.5 MPa, producing floor tile specimens measuring 12x6x1 cm. Thereafter, specimens were fired at kiln temperature of 1000^{o}C and 1100^{o}C. Results showed that the inclusion of ISSA, to some extent, affected the engineering properties (shrinkage, water absorption and bending strength), and the addition of nano-SiO_2 showed positive influences on the improvement of engineering properties for both tile specimens. Care should be taken in evaluating the ideal proportions of clay and ISSA and kiln temperature.

2.2.5.2 Lightweight construction materials

Lightweight cement based construction materials can be produced by partially or fully replacing the natural aggregates with lightweight materials, as well as, by using natural or chemical additives that normally form air voids when reacting with cement. Thus, a number of studies were internationally undertaken to investigate the possibility of using sewage sludge products in cement based mixes and lightweight aggregate for the production of lightweight construction materials.

The possibility of producing lightweight cement-based materials was investigated by Wang et al. (2005). Cement-based mixes containing various ratios of Incinerated Sewage Sludge Ash (ISSA) were tested for their lightweight and engineering properties. The study concluded that ISSA can be used for the production of lightweight materials, as the hydration process generated pores with diameter less than 0.1 µm.

Chiou et al. (2006) prepared spherical particles made from mixes containing Sewage Sludge (SS), ISSA, water and additive. Prepared particles were fired at 1150^{o}C, and were tested for their lightweight properties such as unit weight. Results showed that the use of 20-30% of sewage sludge gave the most adequate lightweight properties.

Wang et al. (2009) produced lightweight aggregate from firing mixes containing thermally Dried Sewage Sludge (DSS) and proportion of Coal Ash (CA) at 1100^{o}C for 3hrs. Five different mixing ratios of CA to DSS were evaluated (0, 10, 18, 25 and 32%). The addition of coal ash would produce small pores size and consequently increase the bulk density and improve compressive strength. Mixes incorporated 18-25% coal ash produced the best lightweight aggregate quality and showed an adequate efficiency on immobilizing heavy metals.

Lightweight aggregate can also be made from mixes containing natural clay, as a main material, and different proportions of dewatered sewage sludge (80-90% water content). Uniform pellets with similar diameter of 5-10mm were made and then sintered at a temperature of 1050-1150^{o}C for 10-20min. The pellets were then tested for their engineering and environmental properties. Results showed that total water absorption for mixes containing sewage sludge was lower than that for those without it; also it was shown that no heavy metals were detected when leaching test was performed (Mun, 2007).

Cheeseman and Virdi (2005) studied properties of lightweight aggregate manufactured from Incinerated Sewage Sludge ash (ISSA) mixed with clay binder. Spherical pellets were formed, and were rapidly sintered in a rotary tube furnace at temperatures between 1020 and 1080^{o}C. Results indicated the potential for manufacturing high quality lightweight aggregate using ISSA with relatively simple processing and low sintering temperature.

2.2.5.3 Soil stabilisation

The potential of utilising sewage sludge products in the remediation processes of contaminated soil and improving poor soil quality was widely investigated. Studies showed an evident improvement in certain engineering and environmental properties as described in the studies below.

Theodoratos et al. (2000) investigated the effectiveness of using sewage sludge to immobilise heavy metals in a contaminated soil. Different proportions of biologically treated sewage sludge (70% water content) were mixed with soil samples, and were tested for Toxicity Characteristics Leaching Procurers (TCLP). Results showed that adding 15% of total weight sewage sludge reduces Pb, Zn and Cd solubility by 84, 64 and 76%, respectively, while the addition of 10% sewage sludge was sufficient to reduce Pb solubility below the U.S. EPA TCLP regulatory limit.

A mixture of ISSA and hydrated lime (L) (4:1 respectively) was used as additives to stabilise a subgrade cohesive soft soil. Five different soil mixes incorporating different proportions of ISSA/hydrated lime (ISSA/L), 0, 2, 4, 8 and 16% of total soil weight, were prepared, and were tested for their unconfined compressive strength and triaxial compression. Results indicated that samples containing ISSA /hydrated lime showed higher unconfined compressive strength of three to seven times more than that of untreated soil. The swelling behaviours were also reduced. Results of triaxial compression test revealed that shear strength parameter rose with the increase of the additives (Lin et al., 2007).

A mix of (ISSA) and cement (C) (4:1 respectively) was added to subgrade cohesive soft soil samples in an attempt to improve some engineering properties such as bearing capacity and swelling. Five soil mixes incorporating various ratios of ISSA/cement (ISSA/C), 0, 2, 4, 8 and 16% of total soil weight, were prepared, and were tested for their unconfined compressive strength and triaxial compression. Results showed that unconfined compressive strength for samples incorporated ISSA/cement was approximately improved by 3–7 times more than that of untreated soil sample. Furthermore, swelling behaviour was also reduced as much as 10–60% for treated samples (Chen and Lin, 2009a).

2.2.5.4 Civil engineering applications

The use of ISSA as an alternative absorbent to fly ash and blast-furnace slag (used in wastewater treatment) was investigated by Pan et al. (2003b). Results showed that ISSA could be efficiently used as an absorbent for copper removal from wastewater with a removal efficiency of greater than 98%.

Zhao et al. (2009) investigated the potential use of ceramic particles made of firing dried sewage sludge, fly ash and sand (1:1:1 by weight) in wastewater treatment process. Produced ceramic particles were used, in this study, as an alternative option to the ceramic particles made of traditional clay. Results showed that the removal efficiencies of chemical oxygen demand and ammonium nitrogen, in sewage sludge-fly ash ceramic particles reactor, were all higher than those of traditional clay ceramic particles reactor

A study was undertaken to examine the possibility of using bottom ashes (resulting from burning dried sewage sludge) as an alternative material to the natural clay used in landfill lining construction. Samples were prepared and tested to determine particle size distribution, Atterberg limits, compaction characteristics, hydraulic conductivity, and shear strength parameters. Results of this study showed that properly compacted and stabilized sewage sludge ashes have the required properties to be used in landfill covers or liners (Okol and Balafoutas, 1998).

2.2.5.5 Cement-based systems

Solidification-Stabilisation technology (SS) was applied to sewage sludge products by mixing it with various binding materials. SS technology refers to a group of clean-up methods that prevent or slow the release of harmful chemicals present in contaminated materials. These techniques usually do not change the chemical composition, but keep pollutants from moving into the surrounding environment. This involves binding the hazardous substances and cement to form a solid block where pollutants are encapsulated and trapped in a hardened mass. This approach has been recently utilised by waste management professionals, environmentalist and engineers to both treat hazardous substances and to produce useful materials that can be used for other applications. A number of studies were therefore undertaken to examine the effectiveness of applying the solidification-stabilisation technology to sewage sludge products for the production of sustainable construction materials. Sewage sludge products included Incinerated Sewage Sludge Ash (ISSA), wet sludge, dewatered sludge and dry sludge.

ISSA is an inorganic materials resulting from the incineration of sewage sludge (dewatered or thermally dried) that arises from municipal wastewater plants. The total quantity of ISSA produced in the UK is approximately 100,000 tonnes per annum (Dunster, 2007). The application of ISSA as cement replacement in cement-based materials was investigated to further understand the impact of partially replacing the main binding materials.

Monzó et al. (1999) used ISSA (15 and 30% of total weight) as a cement replacement in mortars. Prepared samples were tested for their engineering properties, including relative compressive gain (CSGr) and flexural strength gain (FSGr). The results revealed that the sewage sludge ash behaves as an active material, resulting in high compressive strength values in comparison with the control mixes, probably due to the pozzolanic properties of used sewage sludge ashes.

Different proportions of ISSA (10-30% of total weight) were used, by Garcés et al. (2008), as a cement replacement. Engineering properties were tested including workability, compressive strength, porosity and length change. Results showed that the best compressive strength was obtained when 10% substitution was used.

Mortars incorporating higher proportion of Sewage Sludge Ashes (SSA) (25 and 50% cement replacement) were investigated by Cyr et al. (2007), and results showed that the addition of SSA induced short delays of cement hydration and lower compressive and flexural strength. It was also shown that presence of SSA has a long term positive impacts which might be related to its pozzolanic properties. The amount of elements leached from samples incorporating SSA was slightly higher than that from the reference mixes, but with the same order of magnitude.

The workability for mixes containing Sewage Sludge Ashes (SSA) (0-30% cement replacement) was investigated by Monzó et al. (2003). Flow Table Spread (FTS) was measured for mortars with various SSA content. Results showed that the inclusion of SSA decreased the workability, and this was due to the irregular morphology of SSA particles and the high water absorption on SSA particle surfaces.

A study was carried out by Pan et al. (2003a) to investigate the influence of Sewage Sludge Ash fineness on initial & final setting time, workability and compressive strength. Paste samples, incorporating 20% of SSA (fineness of 500-1000 m^2/kg) as a cement replacement, were prepared for this purpose. The results showed that mixes containing finer SSA had longer setting time, better workability due to lubricant effects and morphology improvement, and higher compressive strength.

Liu et al. (2011a) tested unfired brick samples made of dewater sewage sludge (50% water content) and four binders (Portland cement, ground silica cement clinker, alumina cement and slag cement). Samples with different cement/sewage sludge/water ratios were prepared and tested for engineering and environmental properties. Tests included compressive strength, freeze and thaw and leaching test. Results revealed that the compressive strength of samples containing alumina cement was higher than samples with other types, and compressive strength loss, due to freeze and thaw process, was also less than the other types. Safe levels of heavy metals leaching were observed.

Valls (2000) tested mixes containing wet sewage sludge (68% water of total weight), Portland cement and coal fly ash for their initial and final setting times. The study mainly concluded that the greater the proportion of sewage sludge the greater the delay in initial and final setting times, as well as, the addition of coal fly ash increased setting time.

Valls (2002) investigated various mixes containing wet sewage sludge (68% water content), Portland cement, sand and water with either fly ash or an accelerating agent ($CaCl_2$). Prepared mixes were tested for their engineering and environmental properties. Results generally showed that the greater the amount of sewage sludge the less the values of compressive strength, with higher compressive strength values for samples without fly ash compared to those containing it. Additionally, results showed high degree of heavy metal retention in all mortar mixes, which ranged between 84-100%.

Malliou et al. (2007) prepared mortar mixes incorporating wet sewage sludge (74% water content), Portland cement, sand, calcium chloride and calcium hydroxide. Specimens were tested for their engineering and environmental properties. Results showed that the greater the amount of sewage sludge the less the compressive strength values. It was also noted that samples containing calcium chloride had an improved compressive strength, and the best results were observed for samples containing 3% $CaCl_2$ and 2% $Ca(OH)_2$. The inclusion of sewage sludge prolonged setting time, and therefore it was recommended to add acceleration agents to reduce setting time. The results showed , high degree of heavy metal retention, which ranged between 0 and 100% with best results given from mixes containing sewage sludge, 3% $CaCl_2$ and 2% $Ca(OH)_2$.

Jianli et al. (2010) used Magnesium Oxychloride Cement (MOC) as a main binder to stabilize wet sewage sludge (85% total water content). Five mixes incorporated different ratios of the above materials were prepared. Testing included the unconfined compressive strength after 10-day curing time, initial and final setting time, and toxic leachability. The study showed that the compressive strength improved constantly with the increase of MOC, with best result obtained for mix containing 20:100 MOC/sludge respectively. Also the initial and final setting times were shorter after increasing the amount of MOC. The study also concluded that heavy metal retention capability improved with increasing the proportion of MOC.

A study was undertaken by Cheilas et al. (2007) to investigate the effectiveness of applying solidification/stabilisation technology to wet sewage sludge (78% water content) by mixing it with Portland cement, sand and Jarosite/Alunite (JA). Two curing types were applied, traditional and Autoclave treatment (16 bar for 3hrs at 200^{o}C). Samples were then tested for their engineering and environment properties. Results showed that compressive strength for samples with Jarosite/Alunite (JA) was generally less than that for samples without it. The results also showed high degree of heavy metal retention in both samples (with and without JA) when Toxicity Characteristic Leaching Procedure (TCLP) was performed.

Katsioti et al. (2008) used Bentonite/cement mortar to stabilise/solidify wet sewage sludge (66.5% water content) contaminated with heavy metals. Various mixes containing sewage sludge, cement, sand and Bentonite were prepared and were tested for their engineering and environmental properties. Results showed that compressive strength was significantly affected by the addition of Bentonite, as samples without Bentonite showed higher compressive strength. The results also showed high degree of heavy metal retention when Toxicity Characteristic Leaching Procedure (TCLP) was performed.

Physical and mechanical properties of concrete mixes with sewage sludge (15% water content) were determined. Four different mixes incorporating Portland cement, sand, coarse aggregate and water with different ratios of dry sewage sludge (0, 2.5, 5 and 10% of total binder weight) were tested for their engineering properties. Results showed that samples with more sewage sludge proportion gave less density, less compressive strength and less flexural strength (Valls et al., 2004). Durability properties for concrete samples containing materials stated above were also examined. A number of durability tests were performed including combined wet–dry cycles using fresh water, seawater and water containing 5% sulphates. Accelerated ageing in an autoclave and accelerated carbonation was also performed. The study concluded that samples with sewage sludge showed acceptable and comparable results to the reference samples (Yagüe et al., 2005).

2.3 FLY ASH

2.3.1 Scope

This section provides detailed information about fly ash properties, production and utilisation. It also briefly discusses the incorporation of fly ash (including rejected fly ash) in the cement-based materials, and its effect on fresh, hardened and durability properties. Properties includes setting time, workability and bleeding, temperature rise, density, length change, density, ultrasound pulse velocity (UPV), strength development, and sulphate resistance.

2.3.2 Fly ash as by-products

Fly ash or Pulverised Fuel Ash (PFA) is a by-product resulting from combusting pulverised coal in coal fired power stations. Fly ash is normally extracted from the furnace gases in the form of fine powder similar to cement or talcum powder fineness. Fly ash particles are typically spherical, ranging in diameters from <1 µm to 150 µm. The type of collection mechanism determines the particles' size. Collected fly ash at older boilers that use mechanical extraction techniques is coarser than ash collected using electrostatic precipitators (Malhotra and Ramezanianpour, 1994).

According to ASTM (ASTM, 2012b), fly ash is mainly classified into three classes: N, F and C. This standard classifies fly ash based on its chemical properties including the minimum content of Silicon dioxide (SiO_2) plus aluminium oxide (Al_2O_3) plus iron oxide (Fe_2O_3), the maximum content of Sulphur trioxide (SO_3), the maximum moisture content and the maximum loss on ignition. It also classifies fly ash based on other physical properties including fineness, soundness and percentage retained on 45µm. In addition to its chemical composition, British Standards (BSI, 2007a) classify fly ash based on loss of ignition values into three main categories: A, B and C. fly ash can also be classified, based on its fineness, into two classes: N and S (Table 2.4). Category C ash is not permitted in UK concrete (BSI, 2012b).

Table 2.4: Classification systems of the US and European standards bodies for fly ash use in concrete (Malhotra and Ramezanianpour, 1994; BSI, 2007a; ASTM, 2012b).

Class	$SiO_2 + Al_2O_3 + Fe_2O_3$(%)	SO_3(%)	Moisture (%)	LOI (%)
ASTM C618				
C	>50	<5	<3	<6
F	>70			<12
BSI				
A	>70	<3	>25	<5
B				2–7
C				4–9

ASTM class F fly ash, which is resulting from burning of harder, older anthracite & bituminous coal ash, is pozzolanic in nature, and contains less lime (CaO) than that of class C. ASTM class C ash is resulting from burning of younger lignite or subbituminous coal, and it is pozzolanic in nature, has some self-cementing properties and contains higher lime (CaO) content.

2.3.3 Mineralogy and chemistry

Fly ash mainly consists of four main components including silica, alumina, ferrous oxide, and calcium oxide with varying amounts of carbon that can be indirectly measured by Loss on Ignition (LOI) test (Ahmaruzzaman, 2010; Blissett and Rowson, 2012). Table 2.5 shows the chemical composition of fly ash from different regions across the globe. In general, the table shows that fly ash has a variety of metal oxides concentrations in the order $SiO_2 > Al_2O_3 > Fe_2O_3 > CaO > MgO > K_2O > Na_2O > TiO_2$. However, chemical composition of fly products showed significant differences not only between regions, but also within the regions themselves (Blissett and Rowson, 2012). Fly ash chemical composition also showed notable differences between different coal types (Table 2.6).

Table 2.5: Chemical composition of fly ash by region.

Component	Range (mass %)					References
	Europe	US	China	India	Australia	
SiO_2	28.5–59.7	37.8–58.5	35.6–57.2	50.2–59.7	48.8–66.0	(Hower et al., 1996; Liu et al., 2004; Moreno et al., 2005; Jankowski et al., 2006; Vassilev and Vassilev, 2007; Kim and Prezzi, 2008; Dutta et al., 2009; Diaz et al., 2010; Mishraa and Dasb, 2010; Liqiang and Yongtao, 2011; Blissett and Rowson, 2012; Yana et al., 2012)
Al_2O_3	12.5–35.6	19.1–28.6	18.8–55.0	14.0–32.4	17.0–27.8	
Fe_2O_3	2.6–21.2	6.8–25.5	2.3–19.3	2.7–14.4	1.1–13.9	
CaO	0.5–28.9	1.4–22.4	1.1–7.0	0.6–2.6	2.9–5.3	
MgO	0.6–3.8	0.7–4.8	0.7–4.8	0.1–2.1	0.3–2.0	
Na_2O	0.1–1.9	0.3–1.8	0.6–1.3	0.5–1.2	0.2–1.3	
K_2O	0.4–4	0.9–2.6	0.8–0.9	0.8–4.7	1.1–2.9	
P_2O_5	0.1–1.7	0.1–0.3	1.1–1.5	0.1–0.6	0.2–3.9	
TiO_2	0.5–2.6	1.1–1.6	0.2–0.7	1.0–2.7	1.3–3.7	
MnO	0.03–0.2	-	-	0.5–1.4	-	
SO_3	0.1–12.7	0.1–2.1	1.0–2.9	-	0.1–0.6	
LOI	0.8–32.8	0.2–11.0	-	0.5–5.0	-	

Table 2.6: fly ash chemical composition by coal type (Ahmaruzzaman, 2010).

Component (wt.%)	Bituminous	Sub-bituminous	Lignite
SiO_2	20–60	40–60	15–45
Al_2O_3	5–35	20–30	10–25
Fe_2O_3	10–40	4–10	4–15
CaO	1–12	5–30	15–40
MgO	0–5	1–6	3–10
Na_2O	0–4	0–2	0–6
K_2O	0–3	0–4	0–4
SO_3	0–4	0–2	0–10
LOI	0–15	0–3	0–5

In addition to the main chemical components above, fly ash contain many other elements that have a concentrations of greater than 50 mg/kg, some of which of real environmental concern (Izquierdo and Querol, 2012). Table 2.7 shows the concentrations levels of trace elements in European fly ashes. They show relatively similar trace element concentrations to those Australian ones. Some trace elements such as As, Cr, Pb, and Se are present in significant quantity and therefore the likelihood for these element to escape to the surrounding environment is high. The leachability of the elements is strongly linked to the phase with which they are associated and other conditions such as pH that they are exposed to (Jankowski et al., 2006).

Table 2.7: Trace elements content in European fly ashes (Moreno et al., 2005).

Element	Trace element composition (ppm)	
	minimum	maximum
As	22	126
B	24	534
Ba	311	3134
Be	3	34
Cd	1	6
Co	20	112
Cr	47	281
Cu	39	254
Ge	1	61
Hg	<0.01	1.4
Li	36	377
Mo	5	22
Ni	49	377
Pb	40	1075
Rb	22	202
Sb	1	120
Se	3	30
Sn	4	15
Sr	131	4406
Th	17	65
U	5	29
V	154	514
Zn	70	924

2.3.4 Fly ash Morphology

The morphology of fly ash particles is mainly controlled by the applied burning temperature and subsequent cooling rate. Scanning Electron Microscopy (SEM) analysis showed that fly ash samples consist of solid spheres, hollow spheres (cenospheres), and irregular unburned carbon (Blissett and Rowson, 2012). Fly ash samples also include mineral aggregates containing corundum, quartz, and magnetite particles (Kutchko and Kim, 2006; Benezet et al., 2008).

There are two modes for the inorganic materials in coal to occur; they are either to be included within the organic particle or excluded completely as separate mineral grains. The formation of fly ash particles is shown in Figure 2.3. The first step of the mineral transformation process is the conversion of the coal to char. High burning temperatures causes the char to fragment, and consequently the fine included minerals gradually reduce and are released from within the char. At this point and as a result of the decomposition process of minerals, gases are formed. Formed gases eventually condense forming solid ash particles. Ash particles between 0.02 and 0.2µm result from the homogeneous condensation, whereas particles between 0.2 and 10µm result from fragmentation of mineral matters present. The excluded mineral matter undergoes a series of complex transformations to form spherical particles range 10–90µm in size (Sarkara et al., 2005). Figure 2.4 shows the typical particle size distribution for a UK fly ash compared to European fly ashes.

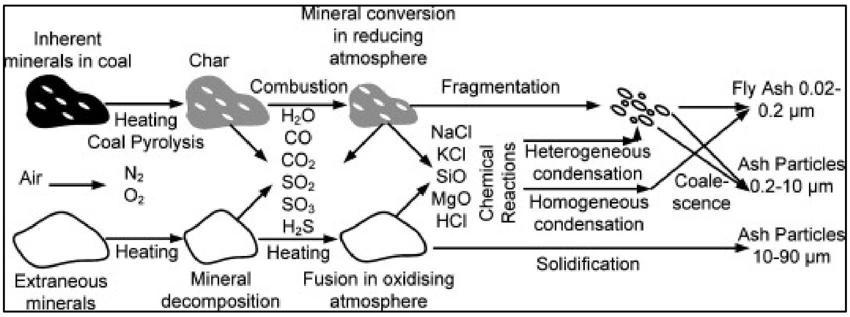


Figure 2.3: Mechanism of fly ash formation from pulverised fuel combustion (Tomeczek and Palugniok, 2002).

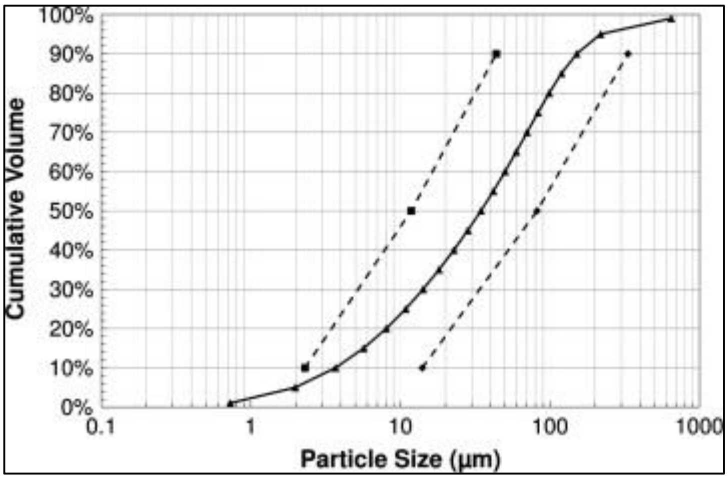


Figure 2.4: Typical particle size distribution of a UK coal fly ash (▲) (Blissett and Rowson, 2012) in comparison to upper (♦) and lower (■) ranges from European coal fly ashes (Moreno et al., 2005).

2.3.5 Fly ash production and utilisation

In the UK, about 5,300,000 tonnes of fly ash and 800,000 tonnes of furnace bottom ash are produced annually. An additional 1,500,000 tonnes of gypsum from the fuel gas desulphurisation systems are also produced. This level of production had been relatively consistent for the last few years; however, it has significantly been reduced in the last two years (Sear, 2011). Figure 2.5 shows the utilisation of ash products in the UK for 2011.

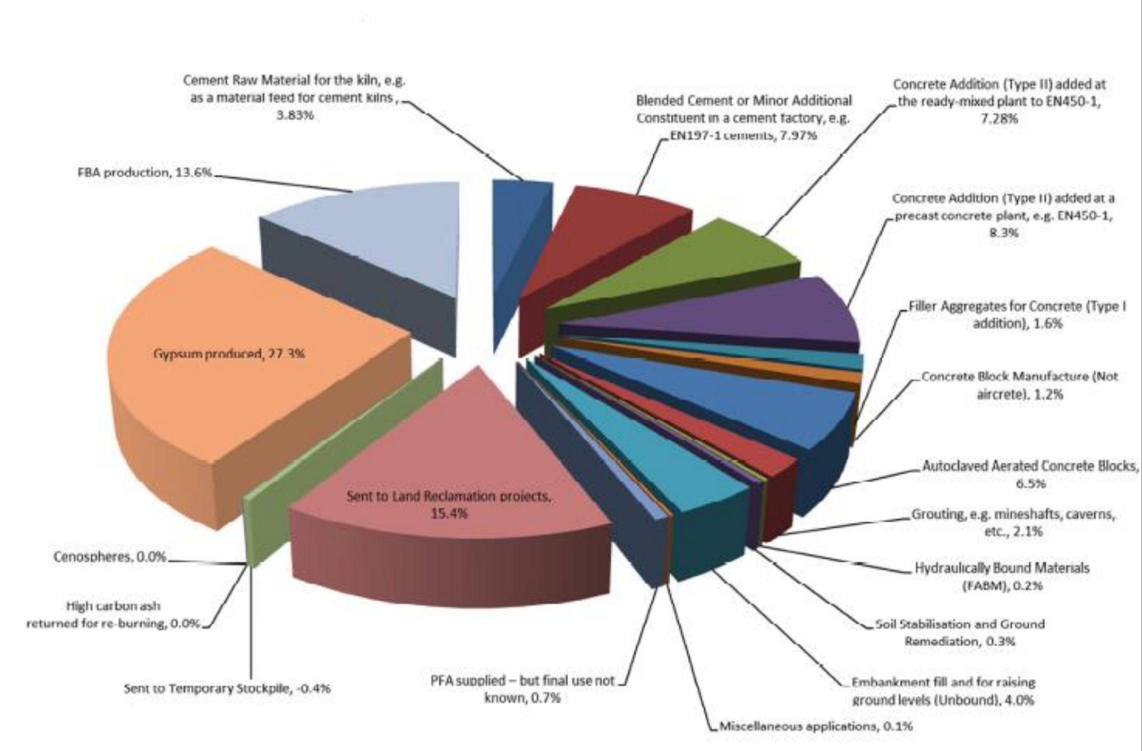


Figure 2.5: Utilisation of ash products in the UK for 2011 (UKQAA, 2011).

Fly ash products can be used in different application within the construction industry. This includes pre-blended cement, concrete production, fill & grouting, aggregate & filler, road construction and block making (UKQAA, 2013g). Fly ash applications in the construction industry can be summarised as follows:

- **Pre-blended cement:** BS EN 197-1 (BSI, 2011a) states that Portland cement CEM I can be pre-blended with fly ash at different ratios to produce other cement types. Cement types include CEM IIA-V (contains between 6 to 20% fly ash), CEM IVA & VLH IVA (contain 11 to 35% fly ash), CEM IIB-V (contains between 21 to 35% fly ash) and CEM IVB & VLH IVB1 (can contain up to 55% fly ash).
- **Concrete Products:** Fly ash, that complies with BS EN 450 (BSI, 2007a), can also be mixed with Portland cement CEM I on site (mixer-blended fly ash) to obtain concrete products. BS EN450 category S fly ash with a fineness not greater than 12.0% (fly ash retained on the 45µm sieve), and Loss On Ignition (LOI) not greater than 7% (category A or B) can be used in concrete mixes. These requirements are to reduce water demand and to improve reactivity & consistency properties within the concrete. Water reductions values vary between 6 and 12% in comparison with concrete made of CEM I only. This category of fly ash can be used at 25-55% of the cementitious content of concrete. BS EN 206 (BSI, 2000b) and BS 8500 (BSI, 2012a) permit BS EN 450 Category N fly to be used

in concrete products. There is no requirement for water reduction as this effect is closely related to fineness (UKQAA, 2013a).

- **Fill and grout:** According to BS EN 12620 (BSI, 2008a) and BS EN 13055-1 (BSI, 2002c), fly ash can be used as a filler aggregate for precast concrete and grout application. The range of accepted fineness is 70-100% passing the 63µm sieve. These standards assume that fly ash is an inert material without any pozzolanic reactions. However, it will contribute to the strength and durability properties as the reactions occur (UKQAA, 2013a; UKQAA, 2013c).
- **Lightweight aggregates**: Fly ash products can also be used for the production of lightweight aggregate: This type of aggregate is called *"sintered pulverised fuel ash lightweight aggregate"*. Pellets made of fly ash, mixed with controlled ratios of water are formed, and later fired at temperature of 1000-1250^{o}C. The water is driven off resulting in a hard, honeycombed structure of interconnecting voids within the aggregate. The size of manufactured aggregate varies from 14mm down to fines, which then can be graded into a variety of sizes (UKQAA, 2013d).
- **Road construction**: BS EN 14227 (BSI, 2004b; BSI, 2004c; BSI, 2006) and BS EN 13242 (BSI, 2007b) permit the use of fly ash Bound Mixtures (FABM) and soil treated with fly ash (SFA) in road construction. FABM and SFA are mixtures made of fly ash and other constituents mixed with water. These materials have to be compatible with compaction by rolling, and have to rely on the pozzolanic reactions of the fly ash (UKQAA, 2013e).
- **Block making**: Fly ash products can be used, according to BS EN 771 (BSI, 2011b) and BS 3892 (BSI, 1996a; BSI, 1997), in block making (UKQAA, 2013f).

2.3.6 Fly ash products in cement-based systems

2.3.6.1 Cement- based systems

Cement products are the most dominant binding agents used in the construction industry for the production of building materials. Building materials include cement pastes, cement mortar, concrete products, masonry blocks, pavement tiles and finishing products. Portland cement was patented by Joseph Aspdin, a Leeds builder, in 1824. Portland cement is obtained by intimately mixing calcareous and argillaceous, or other silica-, alumina-, and iron oxide-bearing materials, burning them at clinkering temperature and grinding them to produce cement. The production process essentially includes mixing & grinding the raw materials (limestone or chalk, and silica & alumina found in clay or shale), and burring them in a rotary kiln at 1400^{o}C. Sintered materials (clinker) is ground to a fine powder and then mixed with gypsum forming Portland cement. Portland cement is mainly consists of four compounds: Tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium almuminoferrite (Neville and Brooks, 2004). The chemical composition of Portland cement is shown in Table 2.8 and Table 2.9.

Table 2.8: Main compound of Portland cement (Neville and Brooks, 2004).

Compound	Oxide composition	Abbreviation
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Dicalcium silicate	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium almuminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF

Table 2.9: Approximate composition limits of Portland cement (Neville and Brooks, 2004).

Oxide	Content %
CaO	60-67
SiO_2	17-25
Al_2O_3	3-8
Fe_2O_3	0.5-6
MgO	0.1-4
Alkalis	0.2-13
SO_3	1-3

In the presence of water, the silicates and aluminates in Portland cement react and form products of hydration or hydrates, which in time produce the hard mass in cement paste. The two silicate compounds (C_3S and C_2S) react with water and produce $C_3S_2H_3$ (C-H-S gel) and some lime $Ca(OH)_2$; the reaction of C_2S produces less lime. The hydration reaction of C_3A is very fast and can lead to a flash set, which is prevented by the addition of gypsum. The approximate hydration reaction is presented in Reactions 2.1, 2.2 and 2.3 (Neville and Brooks, 2004).

For C_3S:

$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3Ca(OH)_2$ Reaction 2.1

For C_2S:

$2C_2S + 4H \longrightarrow C_3S_2H_3 + Ca(OH)_2$ Reaction 2.2

For C_3A:

$C_3A + 6H \longrightarrow C_3A_6$ Reaction 2.3

2.3.6.2 Fly ash in cement-based systems

The incorporation of fly ash in concrete creates many environmental advantages, as well as, it improves concert’s physical and mechanical properties. The main advantages of using fly ash in cement-based products includes improving long term strength & durability, improving workability, reducing water demand, reducing permeability, which reduces shrinkage and creep, improving resistance to chloride ingress and sulphate attack, reducing hydration temperature, improving concrete cohesion, reducing bleeding rates, improving compaction, and giving better pumping properties.

High-calcium fly ash, which mainly incorporates glass phase and other crystalline phases (including C_2S, C_3A, $CaSO_4$, MgO, free CaO and C_4A_3S), has self-hardening properties. When mixed with water, this type of fly ash produces ettringite, monosulphoaluminate hydrate and C-S-H, which cause the hardening properties. The hydration behaviour of both C_2S and C_3A in fly ash is the same as that in cement, but the formation C-S-H from the glass phase is relatively slower (Ghosh and Pratt, 1981). Low–calcium fly ash has no self-cementing properties and can only hydrate when alkalis and $Ca(OH)_2$ are added. The hydration process of this type can produce C-S-H, C_2ASH_8 and C_4AH_{13}, and hydrogarnet is produced at a later stage. The degree of fly ash hydration is increased in the presence of gypsum because the surface is activated by destruction of the structure of the glass and crystalline phases caused by the dissociation of Al_2O_3 reaction with SO_4^{-2} (Uchikawa, 1986).

2.3.6.3 Setting time

The addition of low-calcium fly ash to cement-based mixes generally slows both initial and final setting times. This may due to the proportion of fly ash, its fineness, and its chemical composition (Davis et al., 1937; Lane and Best, 1982). The setting times for cement-based mixes do not only depend on fly ash content, but also depend on the mix’s ambient temperature at which it was mixed. Mailvaganam et al. (1983) investigated the influence of ambient temperature on the setting times for concrete mixes incorporating 30% fly ash replacement. Results showed that mixes at 5^{o}C demonstrated longer setting time than those prepared at 20^{o}C. The addition of high-calcium fly ash also prolongs setting time in comparison with mixes containing Portland cement only (Ramakrishnan et al., 1981; Naik and Ramme, 1990). Setting times prolong with increasing fly ash content, however chemical additives can be used to speed up both initial and final setting times (Figure 2.6) (Yazici et al., 2005).

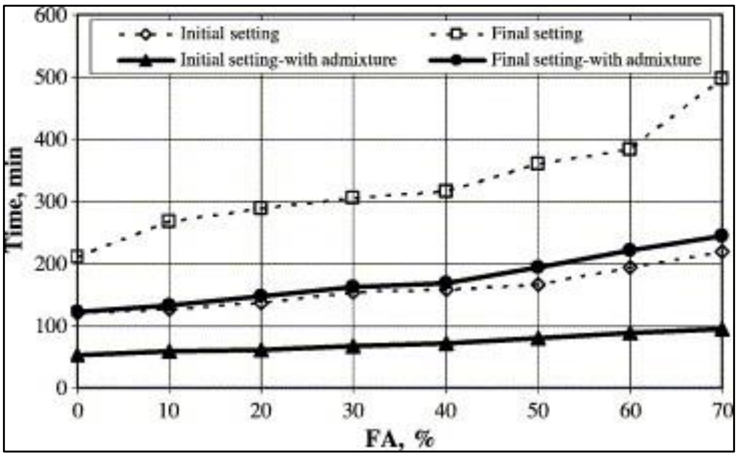


Figure 2.6: The initial and final setting time of cement pastes containing fly ash (Yazici et al., 2005).

2.3.6.4 Workability and bleeding

The addition of fly ash products to cement-based system generally improves workability and reduces water demand in comparison to those mixes made without fly ash. This is due to the small size and essentially spherical shape of fly ash particles (Malhotra and Ramezanianpour, 1994). The workability is mainly influenced by the proportion of coarse materials (>45µm) in fly ash (Owens, 1979), as workability decreases with increasing the coarse proportion in fly ash. Figure 2.7 shows the effect of coarse fly ash particles on the water requirements.

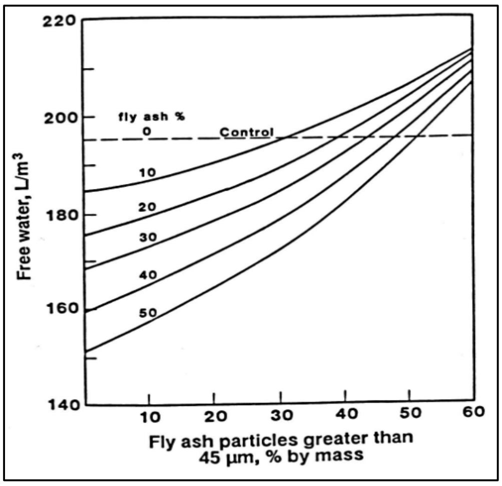


Figure 2.7: The effect of coarse fly ash particles on the water requirements (Owens, 1979).

Additional factor that influences the workability of fly ash concrete is the Loss On Ignition (LOI) value, as it is related to the unburned carbon amount in fly ash. The porous carbon particles absorb hydration water resulting less workability (Brink and Halstead, 1956; Welsh and Burton, 1958; Minnick et al., 1971; Rehsi, 1973).

Concrete with fly ash generally showed reduced segregation and bleeding and it is more efficient when placed by pumping than plain concrete (Central Electricity Generating Board, 1967; Johnson, 1981; Copeland, 1982). This is due to the fine content (spherical shape of particles) in fly ash that improves mix consistency and provides butter finishing surfaces. Figure 2.8 shows relative bleeding of control and fly ash concrete.

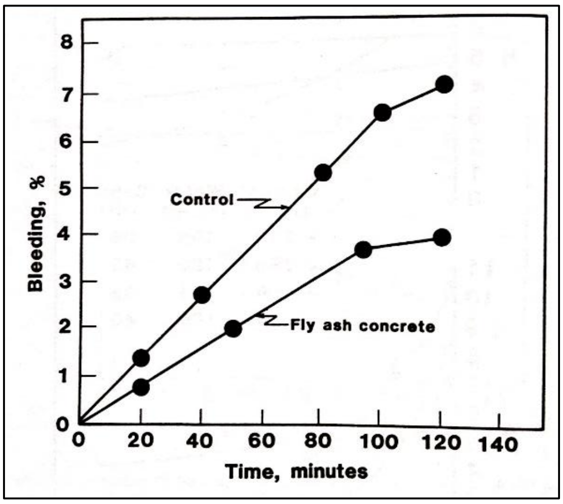


Figure 2.8: Relative bleeding of control and fly ash concrete (Central Electricity Generating Board, 1967).

2.3.6.5 Temperature rise

The hydration process of cement paste is accompanied by the generation of heat that causes a temperature rise in concrete. Temperature rise is of particular importance in mass concrete, where differences in temperature between inner and outer shale occur. This leads to cracks to develop as a result of the internal thermal stress.

The early use of fly ash in concrete was in the construction of a gravity dam to particularly reduce temperature rise (Philleo, 1967). The addition of fly ash (and other pozzolanic material such as calcined diatomaceous shale and ground granulated blast furnace Slag (GGBS)) to concrete products generally reduces hydration temperature. Figure 2.9, Figure 2.10 and Figure 2.11 show the reduction in hydration temperature due to use of various ashes in concrete products.

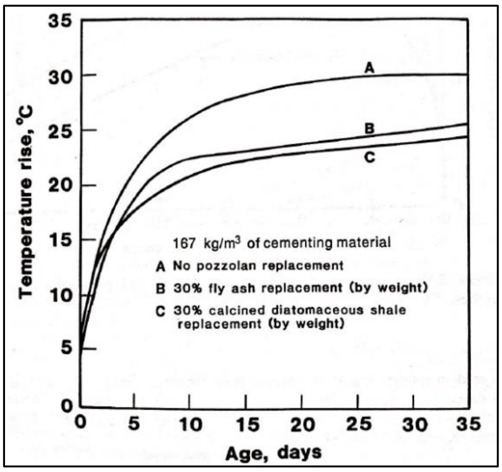


Figure 2.9: Influence of pozzolans on the temperature rise in concrete (Elfert, 1973).

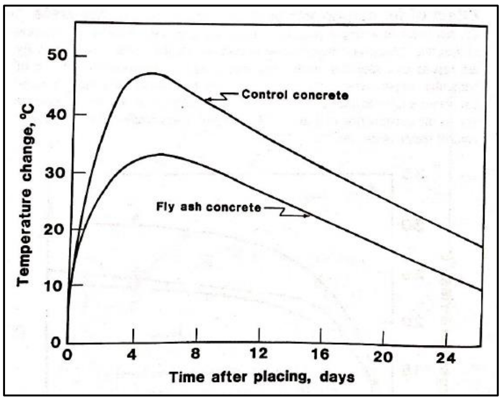


Figure 2.10: Temperature rise curve for 30% replacement fly ash concrete and control concrete (Compton and Macnis, 1952).

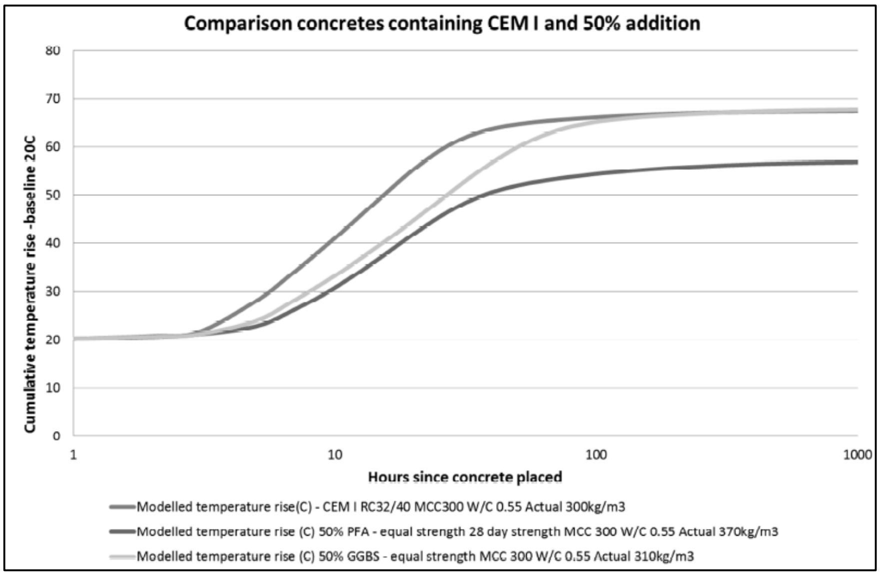


Figure 2.11: Temperature rise for various cementitious types (UKQAA, 2013b).

Temperature rise in concrete does not only depend on the hydration heat, but also depends on other factors including the rate of heat exchange, and thermal properties of used concrete and its surroundings. Figure 2.12 shows the effect of element size and ash replacement on the temperature rise.

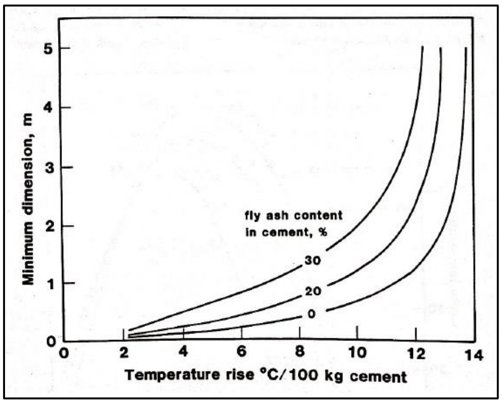
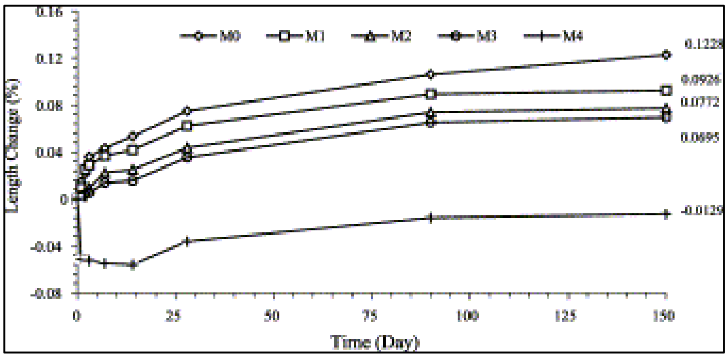


Figure 2.12: The effect of element size and fly ash replacement in temperature rise (Williams and Owens, 1982).

2.3.6.6 Length change

Some studies showed that the addition of fly ash to concrete products generally decreases the drying shrinkage. This may be due to the presence of fine particles in fly ash (particles size < 45μm), which act as filling materials that lower permeability. Figure 2.13 shows the reduction in shrinkage with the addition of fly ash (Atis et al., 2004). Using different curing system still showed less shrinkage change for mortar samples containing fly ash (Figure 2.14) (Yazici et al., 2005). Another study concluded that the addition of fly ash reduces length change not only in Portland cement concrete, but also in other cement types such as Magnesium Oxychloride Cement (MOC) as shown in Figure 2.15 (Chau et al., 2009).



Fly ash replacement %: M0=0, M1=10, M2=20, M3=30 and M4=40

Figure 2.13: Length change of mortar produced versus time (Atis et al., 2004).

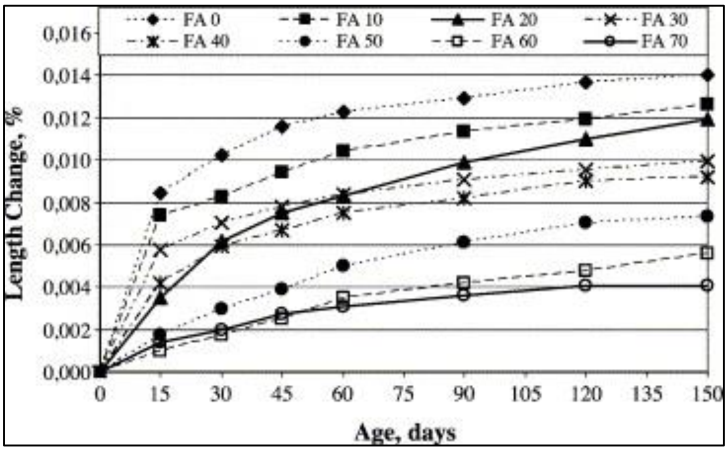


Figure 2.14: Length changes of steam-cured mortar specimens with different fly ash ratios (Yazici et al., 2005).

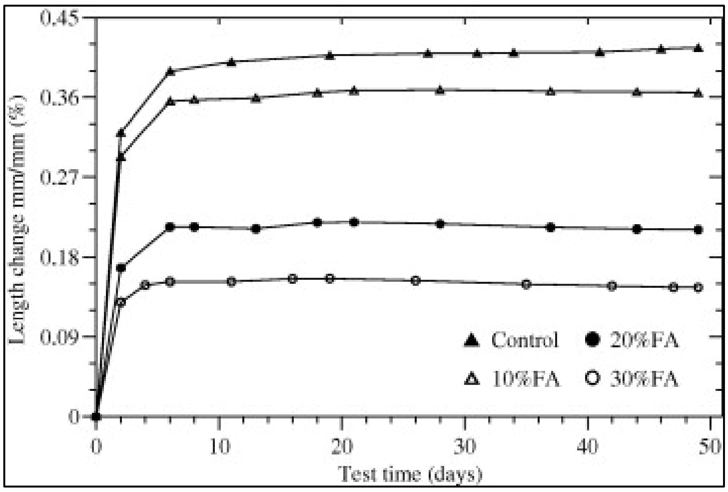


Figure 2.15: Drying shrinkage of the MOC mortars with different contents of fly ash (Chau et al., 2009).

On the other hand, other studies showed that the replacement of cement with fine fly ash does not influence drying shrinkage for cement-based materials. Haque and Kayali (1998) studied the influence of including class F fine fly ash with 99% passing through a 45µm sieve in concrete throughout six main mixes. Mixes contained a constant binder content of 400 and 500 Kg/m^3, and three replacement ratios at 10, 20 and 30% of fly ash. Results showed no significant differences in drying shrinkage between plain concrete and fly ash concrete (Figure 2.16).

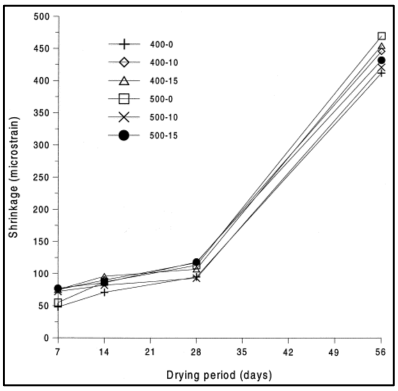


Figure 2.16: Drying shrinkage of the concretes tested (Haque and Kayali, 1998).

Replacing cement with higher volume of fine fly ash also showed no major differences in drying shrinkage between plain concrete and that with fly ash. Baoju et al. (2000) replaced cement with 51% Ultrafine Fly Ash Composite (UFAC), with a surface area of about 740 m^2/kg. Results showed a similarity in drying shrinkage for both plain and fly ash concrete, as shown in Figure 2.17.

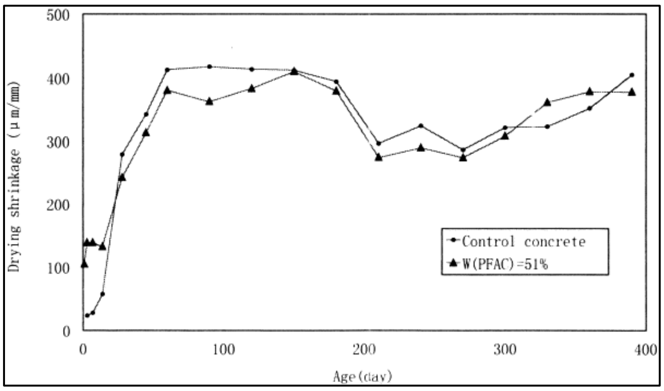


Figure 2.17: Drying shrinkage for plain concrete and UFAC concrete (Baoju et al., 2000).

2.3.6.7 Density

The addition of fly ash to cement-based materials generally reduces density, as fly ash has a lower relative particle density (2.30 typically) than Portland cements (3.12 typically). Replacing 30% of cement mass with fly ash increases the total volume of cementitious material by 15% (UKQAA, 2013a).

Uygunoglu et al. (2012) investigated the influence of incorporating fly ash in Pre-fabricated Concrete Interlocking Blocks (PCIBs) that were made of Portland cement and three types of aggregates. Aggregates included crushed sand stone (CSS), marble waste (MW) and concrete waste (CW) aggregates (specific gravity of 2.65, 2.70 and 2.24, respectively).

Cement was replaced with fly ash at 10, 20, 30 and 40%. Results showed that blocks density decreases with increasing fly ash content (Figure 2.18).

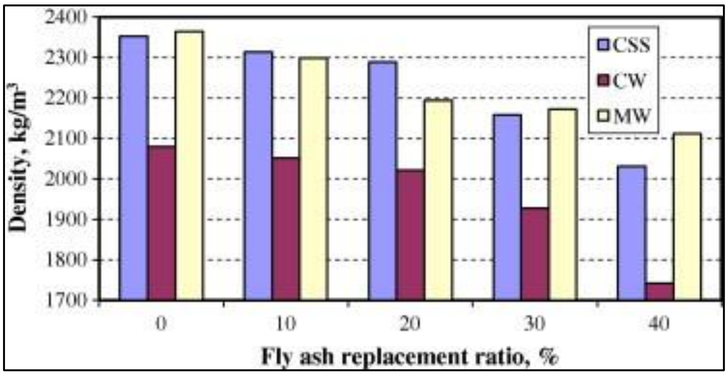


Figure 2.18: Density of PCIBs (Uygunoglu et al., 2012).

Lam et al. (2007) studied the use of fly ash for the production of concrete paving blocks made of Portland cement, sand, Recycled Crushed Glass (RCG) and Recycled Concrete Fine (RCF) aggregates. Constant cement to aggregate ratio of 0.44 was used, and four different ratios of fly ash (0, 10, 15 and 20% by weight) were added. Results showed a reduction in block density when the fly ash content was increased (Figure 2.19).

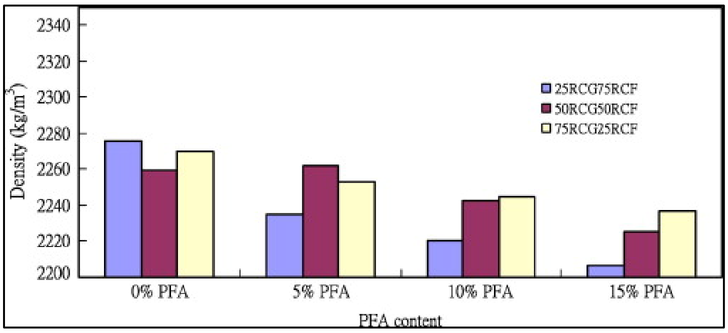


Figure 2.19: Results of density of concrete paving blocks prepared with different glass and fly ash content (Lam et al., 2007).

Older concrete specimens incorporating fly ash exhibited no significant differences in density in comparison with younger ones. Camilleri et al. (2006) investigated engineering properties of concrete mixes incorporating different ratios of fly ash (0, 10, 20, 35 and 50% cement replacement). The used materials were mixed with the following proportions: cement: 362, water: 210, fine aggregate: 794, and coarse aggregate: 861 kg/m3. The water/cement ratio was set at 0.58 and slump at 30–60 mm. Results showed that dry concrete density reduces with increasing fly ash content (Figure 2.20).

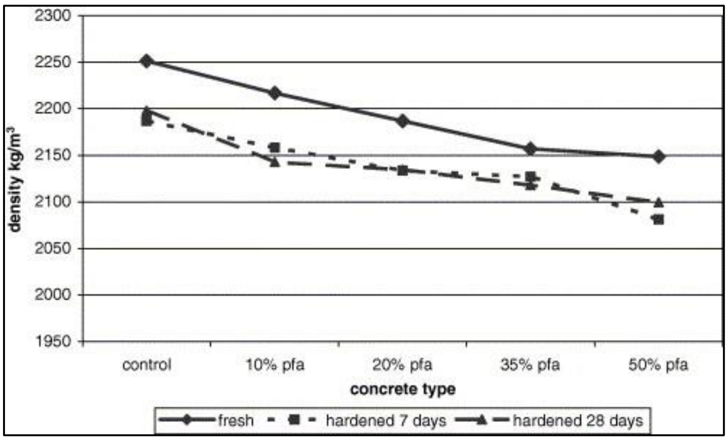
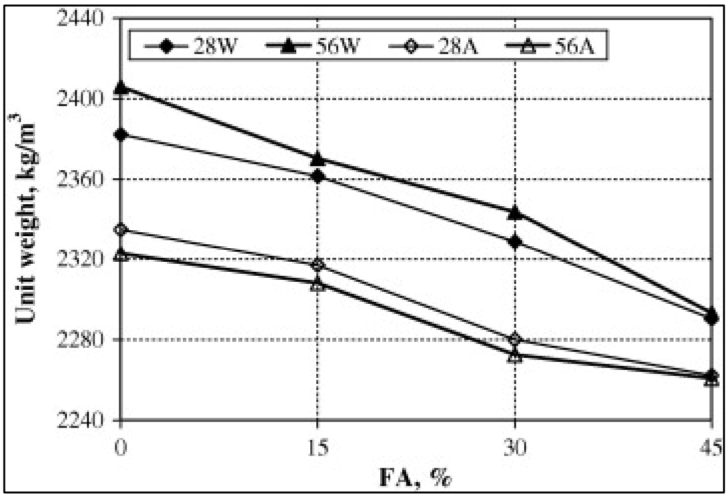


Figure 2.20: Fresh and hardened density of concrete with various ratios of cement replacement with fly ash (Camilleri et al., 2006).

The curing regime of concrete samples did not show any differences in density between plain concrete and fly ash concrete, as and regardless of the curing regime, density of concrete samples decrease with increasing fly ash proportion. Bog and Topçu (2012) investigated the influence of applying two curing regimes, air and water, on engineering properties of concrete samples incorporating different ratios of fly ash (0, 15,30 and 45% cement replacement). Samples were cured for 28 and 56 days. Figure 2.21 shows the relation between unit weight of concrete samples with different fly ash ratios and different curing regimes.



A is air curing and W is water curing.

Figure 2.21: The variation in concrete unit weights with respect to fly ash ratio (Bog and Topçu, 2012).

2.3.6.8 Ultrasonic Pulse Velocity (UPV)

UPV in a non-destructive test used in concrete and other solid construction materials to examine its quality and compressive strength. It employs an ultrasonic pulse to provide information on the uniformity of concrete, cavities, cracks and defects. The pulse velocity in any construction material depends on its density and its elastic properties. Concrete quality can be classified based on UPV values: >4.5 km/sec is strong, 3.5-4.5 km/sec is good, 2-3.5 km/sec is intermediate, and <2 km/sec is weak (Whitehurst, 1951). Figure 2.22 shows UPV values for different concrete types.

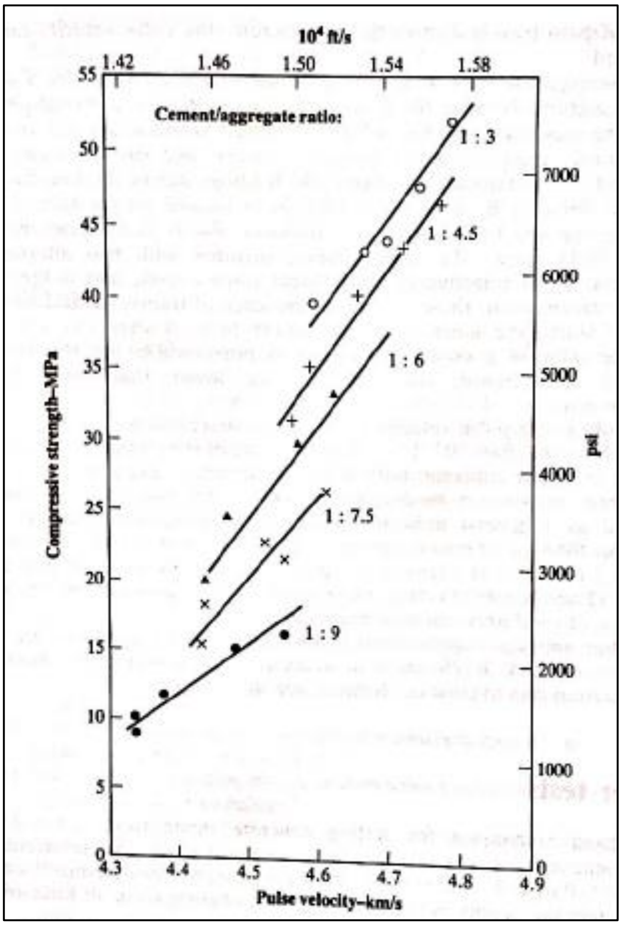


Figure 2.22: UPV values for different concrete types (Jones and Gatfield, 1955).

As UPV is a function of strength and porosity. It was shown that UPV values decrease with increasing w/c ratios. Al-Mufti and Fried (2012) investigated the influence of varying w/c ratios for concrete mixes on UPV. The UPV values were found to decrease with increasing w/c ratio for both fresh and hardened concrete (Figure 2.23).

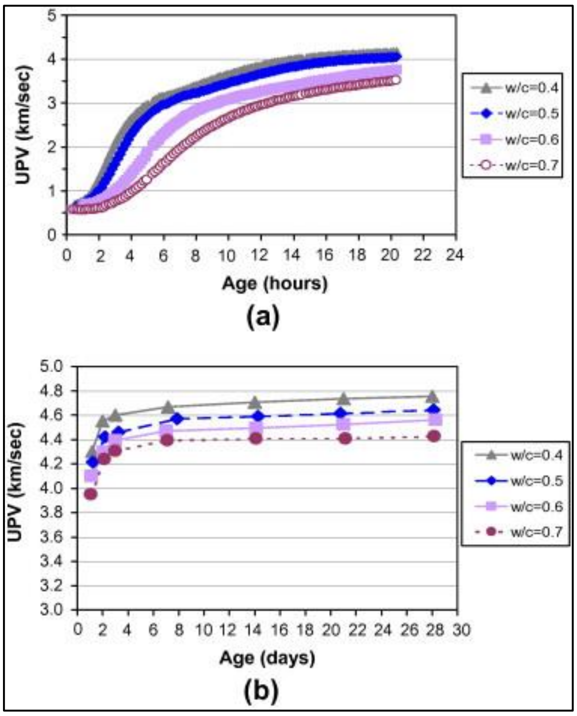


Figure 2.23: UPV variation at early age for normal concrete with varying water/cement ratios: (a) for fresh concrete and (b) for hardened concrete (Al-Mufti and Fried, 2012).

Liu et al. (2011b) investigated the influence of varying w/c ratios in cement paste on UPV at earlier stages. Three w/c ratios were used (0.23, 0.35 and 0.53) and were tested for their UPV at early ages (up to 3000min). Results demonstrated that UPV is decreasing with increasing w/c ratios, as shown in Figure 2.24. Their study also included the influence of varying fly ash, ASTM Class F fly ash, content in cement passed on UPV. Cement was replaced with fly ash at 0, 10, 30 and 50%. The UPV values decreased with increasing fly ash content (Figure 2.25).

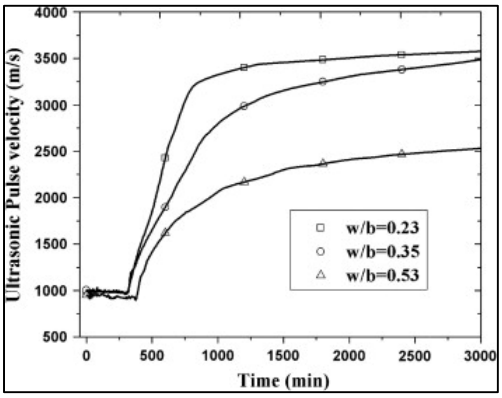


Figure 2.24: Influence of w/binder on UPV (Liu et al., 2011b).

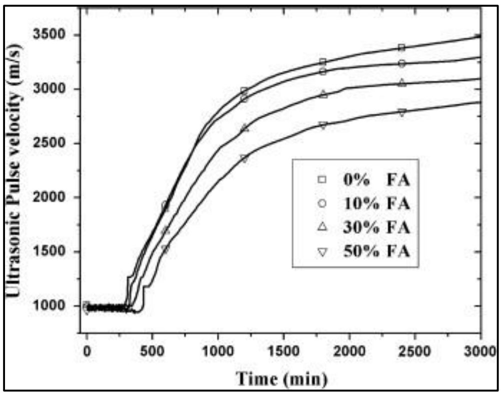


Figure 2.25: Influence of fly ash content on UPV (Liu et al., 2011b).

The addition of fly ash to concrete mixes generally reduces the UPV values. Topcu and Canbaz (2007) investigated the influence of adding class F fly ash to concrete mixes incorporating three types of fibers. Fibers included Steel Fibres (SF), and two types of Plastic Propylene Fibers (PPI and PPII). Cement was replaced with 10, 20 and 30% fly ash (by weight). Cylindrical concrete samples, incorporating Portland cement, fine aggregate, coarse aggregate, fibers, water and fly ash, were prepared and cured for 28 days. The results showed that the increase of fly ash content led to a reduction in the UPV values (Figure 2.26).

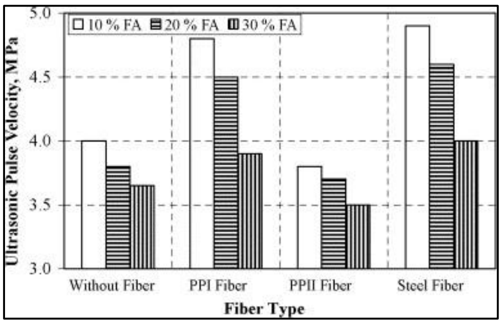
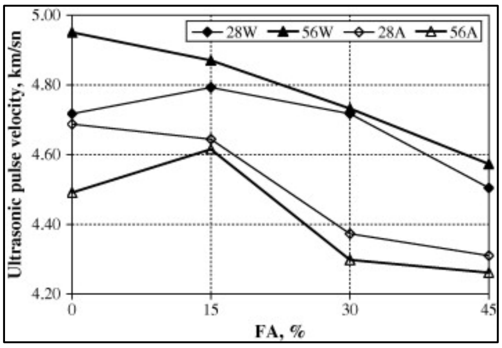


Figure 2.26: Ultrasonic pulse velocity versus fiber content and fly ash replacement ratio (Topcu and Canbaz, 2007).

UPV values of concrete do not depend on fly ash amount only, but also depend on other factors including curing regime and duration. Bog and Topçu (2012) investigated the influence of applying two curing regimes, air and water, on UPV of concrete samples incorporating different ratios of fly ash (0, 15, 30 and 45% cement replacement). Samples were cured for 28 and 56 days. Figure 2.27 shows the relation between UPV values of concrete samples with different fly ash ratios and curing regime. Generally, the UPV decreases with increasing amounts of fly ash. Water cured specimens gave higher values than those which were air cured. This may be due to the availability of water, thus allowing the pozzolanic reaction to continue.



A is air curing and W is water curing.

Figure 2.27: The variation in concrete ultrasonic pulse velocities with respect to fly ash ratio (Bog and Topçu, 2012).

2.3.6.9 Compressive strength

Compressive strength is one of the most important structural properties of concrete, which mainly depends on cement content, water to cement ratio and aggregate quality (and quantity). Long-term compressive strength of cement-based systems can be improved by including fly ash due to pozzolanic activities (Bouzoubaa et al., 1998; Lam et al., 1998; Poon et al., 2000; Kearsley and Wainwright, 2001; Escalante-García and Sharp, 2005; Siddique et al., 2008). The strength development of fly ash concrete is influenced by a number of variables including the properties of fly ash such as chemical composition, particle size, reactivity, temperature and curing conditions (Malhotra and Ramezanianpour, 1994).

Yuan and Cook (1983) studied the strength development of concrete with and without high-calcium fly ash (CaO=30.3 wt %). The study showed that the rate of strength development of fly ash concrete is comparable to the control mixes, with or without air entrainment (Figure 2.28).

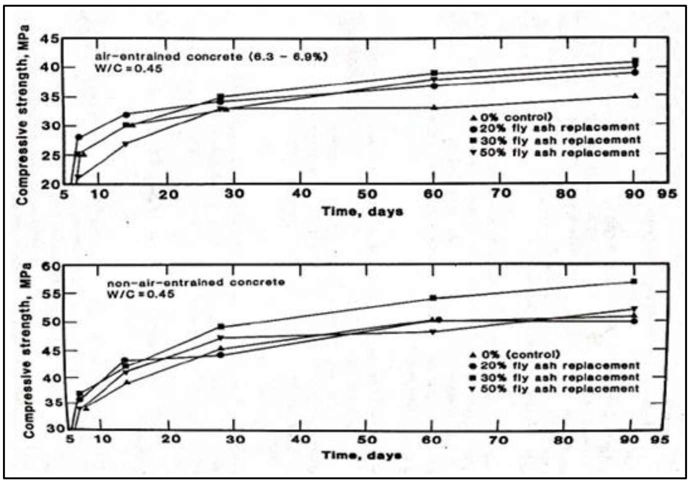


Figure 2.28: Compressive strength development of concrete with and without high-calcium fly ash (Yuan and Cook, 1983).

Gebler and Kleiger (1986) and Tikalsky et al. (1988) examined the effect of fly ash class on strength development in concrete mixes incorporating class C or class F fly ash. The study concluded that the influence of fly ash class on long-term strength development was not significant; however, the addition of fly ash to concrete mixes positively affects strength development. On the other hand, recent studies showed that fly ash class has a significant impact on strength development with time. Sumer (2012) investigated the impact of fly ash class on strength development by using Turkish class C (15.1% CaO) and class F (1.55% CaO) fly ash. 36 mixes, incorporating three different cement contents (260, 320, 400 kg/m^3) with two different ratios (10% and 17%) of reduced cement from the control concretes, were prepared. Cement was replaced by either class C or class F fly ash. Water/binder ratio was added in such a way to maintain a constant slump values between 140–170mm. Compressive strength tests were carried out on 150mm in size cubes. Specimens were cured in lime-saturated water at 20^{o}C and 65% RH. The compressive strength for concrete mixes with class C fly ash demonstrated higher strength than that of the control mixes while class F fly ash concrete mixtures exhibited lower compressive strength than that of the control.

Including higher proportions of fly ash in cement-based system and its impact on both short-term and long-term strength development was investigated. Hannesson et al. (2012) studied the influence of including different types of fly ash and blast furnace slag on the compressive strength of self-consolidating concrete. A total of 21 mixes were cast. Cement was replaced with two sources of fly ash, Boardman FA (28.2% CaO) and Centralia FA (13.6% CaO), and two sources of blast furnace slag, Seattle slag (45.3% CaO) and St. Mary's slag (39.2%CaO), at 0, 20, 40, 60, 80 and 100 wt% (cement replacement). It was observed that the early-age compressive strength (⩽14 days) for all slag mixes was less than the control mix. For the fly ash mixes, the early-age strength was less than the control mixture for replacement of 40% and higher. For later ages (>56 days), both SL and FA mixes with 60% and less replacement had similar or higher compressive strength than the control mix (Figure 2.29). Both trends can be explained by delay in calcium–silicate–hydrate (C–S–H) formation since the pozzolanic reaction becomes the major reaction as the cement replacement increases.

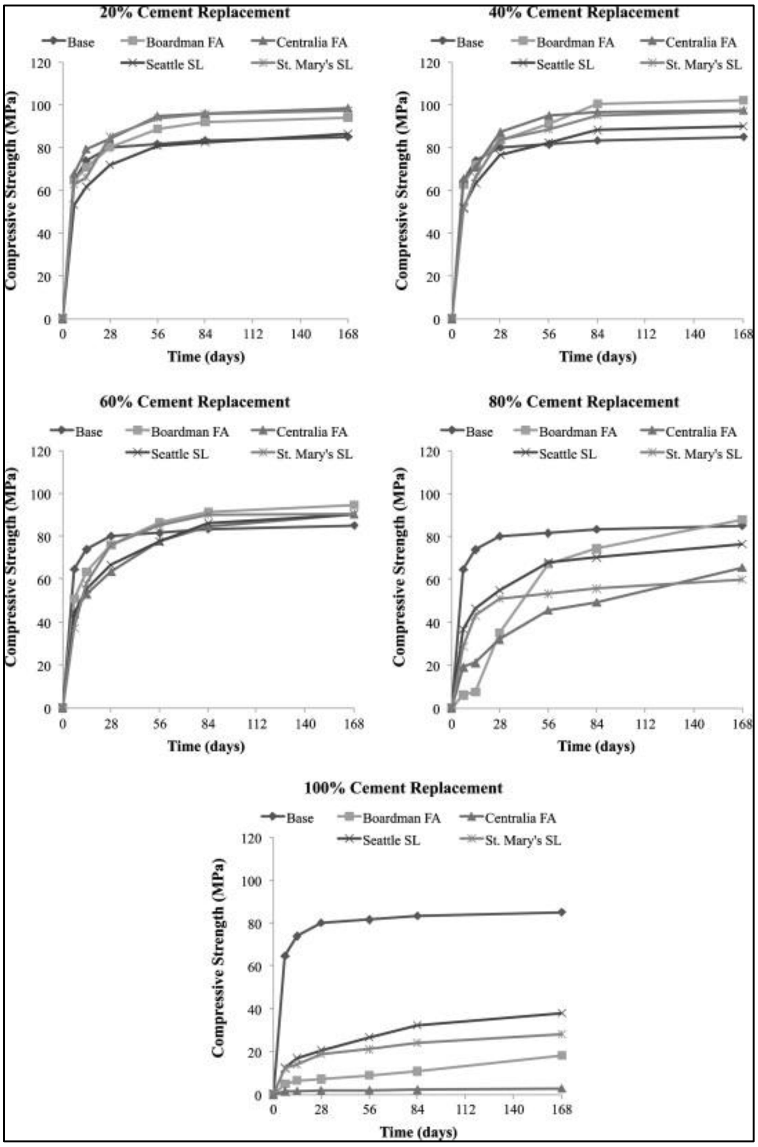


Figure 2.29: Compressive strength gain of the self-consolidation concrete mixes compared to the control mix at 20, 40, 60, 80 and 100% replacement levels (Hannesson et al., 2012).

Poon et al. (2000) undertook a study on high strength concrete prepared with large volumes of low calcium fly ash. Cement was replaced with 0, 25 and 45 (% total weight) class F low calcium fly ash (<3% CaO). Superplasticizer was added to mixing water at different ratios staring from 18.4-33.8 l/m^3. Specimens were cured in water at 27^{o}C until testing (3, 7, 28 and 90 days). Results showed that at w/b of 0.24, the mix with 25% fly ash replacement demonstrated slightly lower compressive strength at 3 and 7 days, but higher compressive strength at 28 and 90 days, when compared to the reference mix. The mix with 45% fly ash replacement showed 8% lower compressive strength than that of the reference mix at 28 days. The negative effect of using fly ash on concrete strength appeared to be insignificant. However, lowering the w/b ratio to 0.19 did not further improve the concrete strength (Figure 2.30).

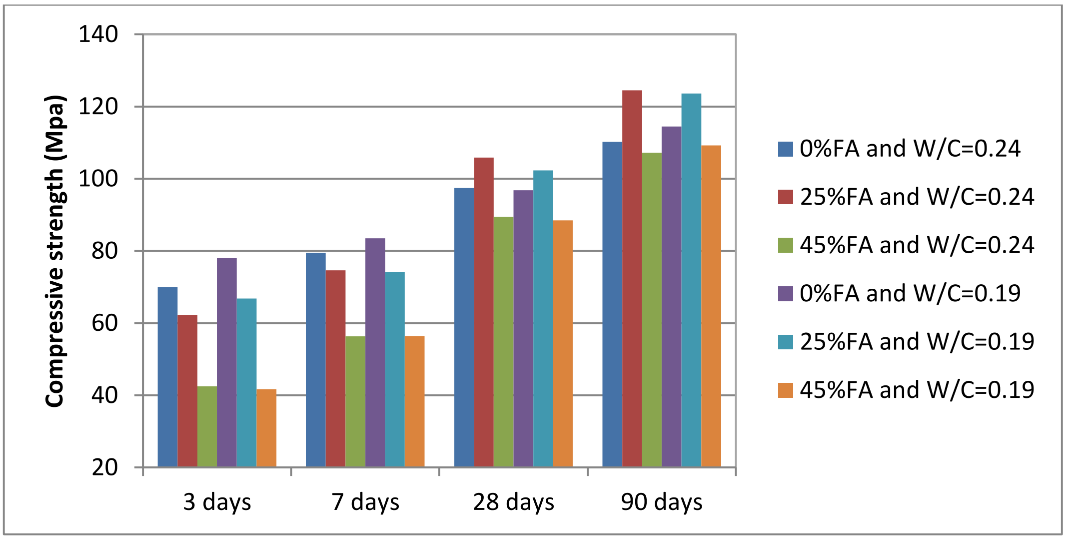


Figure 2.30: Compressive strength of the concrete mixes-graph developed based on compressive strength results by Poon et al. (2000).

Strength development in fly ash concrete is not only dependant on the properties of used materials, but also depends on the applied curing condition. Ramezanianpour (1995) investigated the influence of different curing conditions on the properties of concrete incorporating fly ash, slag and silica fume. Curing conditions included standard moist curing following demoulding, curing at room temperature after demoulding, curing at room temperature after two days of moist curing, and curing at 38°C and 65% RH. Six concrete mixes were examined. In two mixes, cement was replaced with 25 and 58% fly ash (by weight). In another two mixes, cement was replaced with 25 and 50% (by weight) slag, and the last mix incorporated silica fume as cement replacement. The control mix contained 372 kg/m^3 Portland cement and a W/C ratio of 0.50. The results showed that the less the moist-curing duration the lower the strength, the higher the porosity and the higher the permeability. The strength of the concretes containing fly ash or slag showed more sensitivity toward poor curing than that the control concrete. The sensitivity increased with increasing the amounts of fly ash or slag.

Termkhajornkit et al. (2006) also investigated the influence of applying different curing conditions to fly ash-cement pastes. Specimens, incorporating Portland cement, fly ash, water and superplasticizer were prepared. Cement was replaced with 0%, 25% and 50 % (by weight) low calcium fly ash (CaO=1.3%). Specimens were exposed to water curing for different times including 3 days, 7 days or continuous until testing. Thereafter, samples were placed in a moist storage (60% RH) at a temperature of 20^{o}C until testing. Although samples with 50% fly ash replacement with water curing (W) relatively developed higher strength than the other curing conditions (W-7 and W-3), however, curing condition did not significantly influence compressive strength of cement-fly ash paste (Figure 2.31).

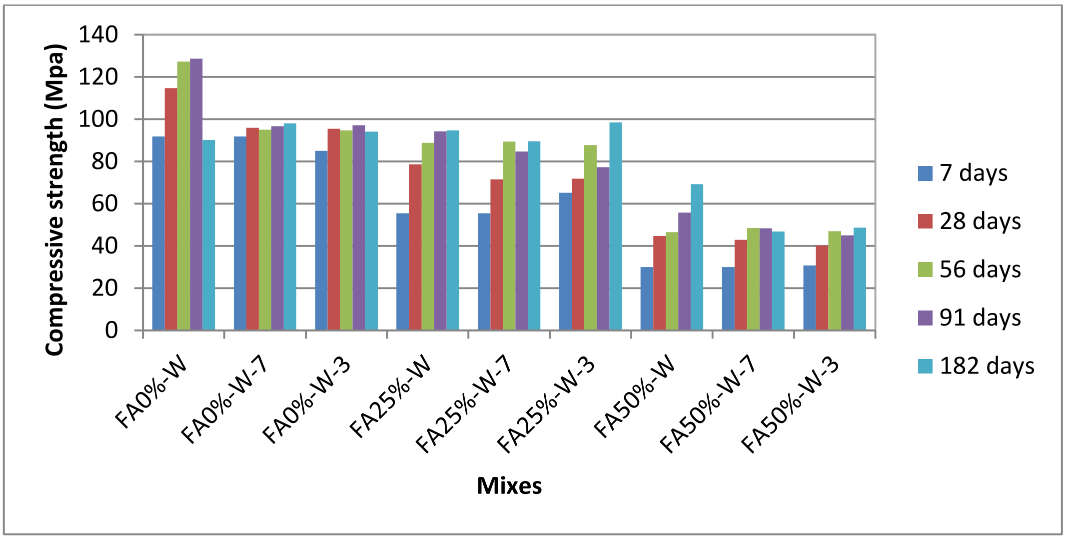


Figure 2.31: Compression strength of fly ash cement paste graph developed based on compressive strength results by Termkhajornkit et al. (2006).

Strength development in cement-based systems containing fly ash is influenced by the particle size of fly ash. Chindaprasirt et al. (2004) investigated the influence of including different particle size fly ash in mortar mixes containing binder: sand ratio of 1:2.75. Water to binder ratios varied between 0.402 and 0.572 to achieve a constant mortar flow of 110±5%. Cement was replaced with 40tw% with one of seven fly ash types: OFA: original fly ash compliant with ASTM C618-Class F, F200: fly ash passed sieve No. 200, F320: fly ash passed sieve No. 325, FF: 10% fine portion fly ash obtained from air separator, FM: 25% medium portion fly ash obtained from air separator and FC: 65% coarse portion fly ash obtained from air separator. Cast specimens were cured in water for 3, 7, 28 and 90 days. The study showed significant improvement in strength development for mortars containing the fine F200, F325 and FF fly ashes, and the medium FM fly ash over that of OFA (Figure 2.32). The reduction in strength development in coarse fly ash mortars may due to the lack of both medium and fine portions, as well as, the increase in water demand because of the rough surface nature of the coarser particles. The fine fly ash with high surface area was more reactive and gave better strength development. The fine fly ash also required less water owing to its spherical shape and smooth surface. The fine portion fills of voids within mortar structure and result an increase in compressive strength.

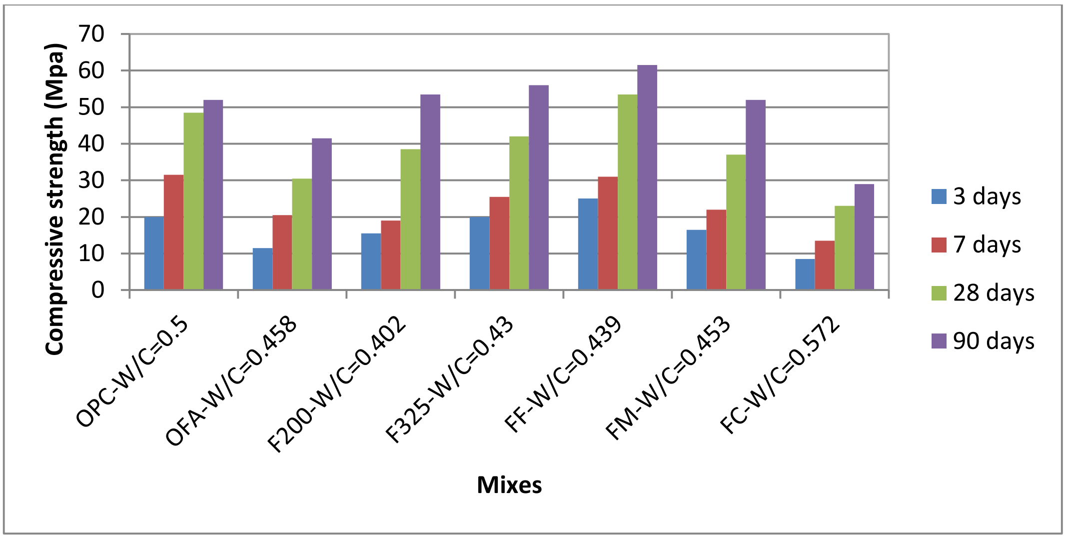


Figure 2.32: Compressive strength of mortar mixes with different particle size fly ash graph developed base on compressive strength results by Chindaprasirt et al. (2004).

2.3.6.10 Sulphate resistance

The incorporation of fly ash products into the cement-based system is well known to positively contribute to sulphate resistance (Dikeou, 1970; Harmann and Mangotich, 1987; Tikalsky and Carrasquillo, 1989; Khatib et al., 2006; Dhole et al., 2009).

Cement hydration process produces comparatively greater amounts of portlandite $Ca(OH)_2$ than both Class C and Class F fly ashes. The reaction of cement hydration products with sulphate is likely to produce more gypsum ($CaSO_4$) and more ettringite ($C3A{\cdot}3CaSO_4{\cdot}32H_2O$), which are responsible for more expansion (Rozière et al., 2009). There are typically two types of sulphate attack: the first one is resulting from the reaction of sulphate with calcium hydroxide to produce gypsum (reaction 2.4); the second type is resulting from the reaction of alumina-bearing hydration products, and/or unhydrated tricalcium aluminate (C_3A) with sulphate and thus ettringite is produced, as presented in reaction 2.5 (Manu et al., 2003).

$Ca(OH)_2+Na_2SO_4.10H_2O \longrightarrow CaSO_4.2H_2O+2NaOH+8H_2O$ Reaction 2.4

$2(3CaO.AL_2O_3.12H_2O)+3(Na_2SO_4.10H_2O) \longrightarrow$
$3CaO.AL_2O_3.3CaSO_4.31H_2O+2AL(OH)_3+6NaOH+17H_2O$ Reaction 2.5

Gypsum can be produced during sulphate attack through cation exchange reactions. The formation of ettringite in hardened concrete, due to sulphate attack, generates internal expansive strain resulting from expansion. Thus the formation of ettringite can lead to cracking and reduced performance, subject to the concrete quality. Sulphate attack through gypsum formation can result in smaller expansion than the ettringite attack, but is more generally known to manifest itself through loss of stiffness and strength (Tian and Cohen, 2000; Santhanam et al., 2002; Monteiroa and Kurtisb, 2003).

In addition to the formation of both ettringite and gypsum and its subsequent expansion, the deterioration of cement-based materials due to sulphate attack is partially caused by the degradation of calcium silicate hydrate (C–S–H) gel through leaching of the calcium compounds. This process leads to loss in stiffness of C–S–H gel and overall deterioration of the cement-based materials (Mehta, 1983). Expansion and cracking are generally attributed to the expansive forces generated by ettringite formation due to the reaction of sulphate with the calcium aluminium hydrates. The loss of weight and strength are generally attributed to reactions where sulphate attacks break down the calcium silicate hydrate (C–S–H), which is the main binding component of hardened cement (Higgins, 2003).

Sumer (2012) investigated the influence of fly ash type on sulphate resistance of concrete specimens. Two Turkish class C (15.1% CaO) and class F (1.55% CaO) fly ash were used. 36 mixes, incorporating three different cement contents (260, 320, 400 kg/m3) with two different ratios (10% and 17%) of reduced cement from the control concretes, were prepared. The reduction in cement content was replaced by either class C or class F fly ash at three different ratios (10, 15 and 20% for 10% cement reduction and 17, 25 and 34% for 17% cement reduction). Water/binder ratio was added in such a way to maintain a constant slump values between 140–170mm. 70x70x280 mm in size prisms were prepared. Cast specimens were left in the mould for 24 hours until demoulding; thereafter they were cured in water for 28 days. After the 28 days initial curing, half of the specimens were placed in a solution of 15% magnesium sulphate and the other half of the specimens were placed in tap water. Before the specimens were placed in the $MgSO_4$ solution, their length was measured using a digital length comparator. Length of specimens immersed in sulphate solution was recorded on monthly bases and was compare to those immersed in water. Expansion data were presented as differences between the length changes observed in magnesium sulphate solution and those in tap water. Results showed that the expansion of the concretes made with both Class C and Class F fly ashes was less than that of the control concrete.

Chindaprasirt et al. (2007) studied the influence of using fly ash (FA) and Rice Husk Ash (RHA) in mortar mixes on sulphate resistance. A control mix (PC) was made of Portland cement and fine aggregate (sand to binder ratio of 2.75). Four more mixes incorporating either fly ash or rice husk ash at 20 and 40 tw% (FA20, FA40, RHA20 and RHA40) were made. The expansion test was carried out in accordance to ASTM C1012 with 5% sodium sulphate solution. Prisms were required to achieve the strength of 20 MPa before being immersed in the sulphate solution. Thus all mixes, except the mixes with high fly ash and rice husk ash replacement, were cured for 24hours. FA40 and RHA40 mortars were cured 2 and 10 days, respectively, because the strength development of these mortars was relatively slow. Results revealed that the expansion of the PC prism is much larger than those made with either fly ash or rice husk ash (Figure 2.33).

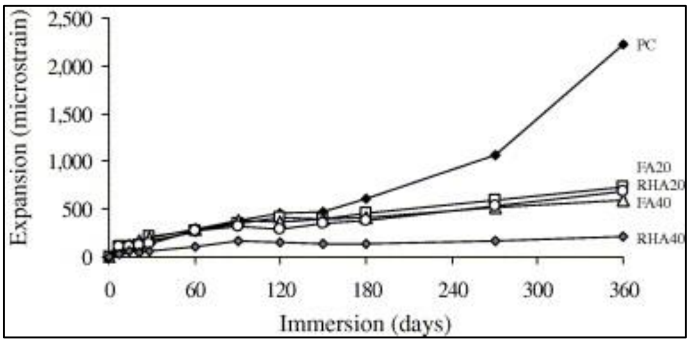


Figure 2.33: Expansion of mortar bars in 5% sulphate solution (Chindaprasirt et al., 2007).

Torii et al. (1995) investigated the influence of including high volume of fly ash in concrete mixes on sulphate resistance. Two series of concrete mixes were designed: the first series was made of 400kg/m^3 Portland cement, fine aggregate, coarse aggregate and two types of fly ash (CaO content was 8.2 and 8.7 wt%). The second series included less cement content of 300kg/m^3. Cement was replaced with both fly ash types at 30 and 50%. 100x100x400 mm prisms were cast and were cured in water at 20^{o}C for 14 days and then stored at 20^{o}C for 14 days under a sealed condition. At 28 days age, specimens were immersed completely in a 10% Na_2SO_4 solution, for the measurements of length change due to sulphate attach. Measurements were taken periodically for two continuous years. Results showed that concrete containing 400 kg/m^3 Portland cement and 50% fly ash replacement was steadily gaining strength, and no detectable deterioration was observed. The influence of fly ash type on the sulphate resistance of high fly ash content concrete was insignificant.

The influence of fly ash particle size on sulphate resistance for mortar mixes was investigated. Chindaprasirt et al. (2004) investigated the influence of including different particle size fly ash in mortar mixes on sulphate resistance. 2x2x285 mm in size mortar bars, compliant with the ASTM C109, were made using ordinary Portland cement (OPC) with sand to binder ratio of 2.75. Six bars were used for each mix. Water to cement ratios varied between 0.402-0.572 to achieve a constant mortar flow of 110±5%. Cement was replaced at 40tw% with one of five fly ash types: OFA: original fly ash compliant with ASTM C618-Class F, F200: fly ash passed sieve No. 200, FF: 10% fine portion fly ash obtained from air separator, FM: 25% medium portion fly ash obtained from air separator and FC: 65% coarse portion fly ash obtained from air separator. The sulphuric acid immersion test was done in accordance with the ASTM C267 using the 5% sulphuric acid solution. Cast specimens were cured in water for 28 days, thereafter specimens were immersed in the 5% sulphuric acid at 23±2°C. The weight loss of the specimens was monitored at 1, 3, 7, 28, 56 and 84 days after immersion. Results showed that the incorporation of the fine fly ash generally reduced the expansion of the mortar bars exposed to the sodium sulphate attack. The fine fly ash reduced water demand for the mortar and thus made it denser as well as stronger. The use of the coarse FC fly ash resulted in an increase in the expansion as water/binder ratio of the FC mortar was relatively high (Figure 2.34).

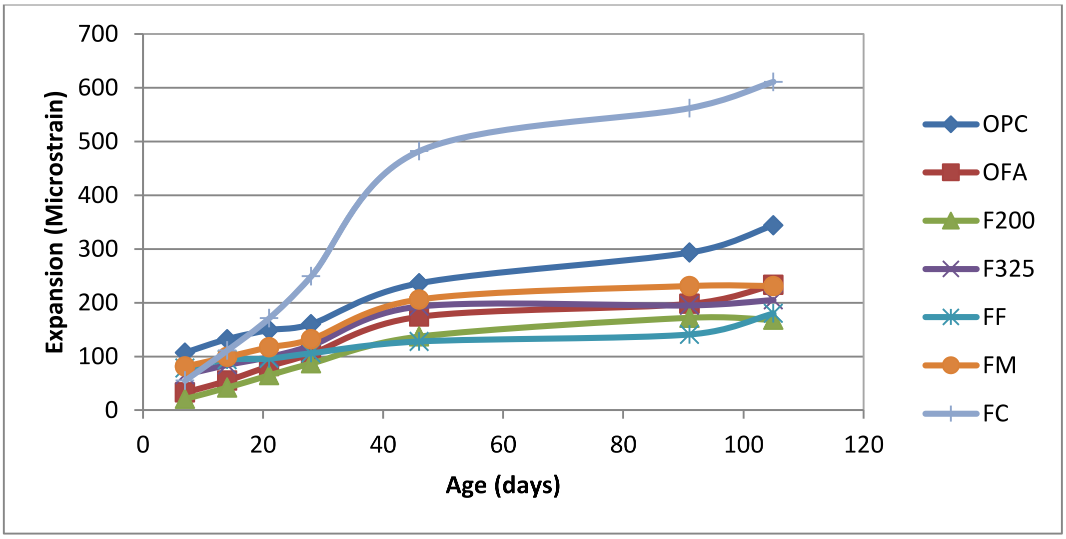


Figure 2.34: Expansion of mortar bar in sulphate graph developed base on expansion results by Chindaprasirt et al. (2004).

2.3.6.11 Unprocessed and rejected fly ash

The American Clean Air Act of 1990 requires a significant reduction in gases released to the atmosphere from power stations. This led to the use of low-NOx burners and catalytic reduction systems in the utility industry. Low-NOx burners and catalytic reduction systems are effective in reducing NOx products; however, they cause an increase in the amount of unburned carbon in the coal ash. This coal ash mainly consists of fly ash with high Loss-On-Ignition (LOI) carbon concentrates (Gray et al., 2002).

The amount of unburned carbon in fly ash is dependent on burner type, burner efficiency, oxygen availability, burning time, pulverized coal particle size and the nature of coal. When a pulverized coal particle is injected into a flame, it decomposes into char and volatiles. The volatiles further decompose to produce soot that creates a luminous zone surrounding the source particles. Char refers to porous, carbon-rich particles that remain in a solid or liquid phase, and soot refers to carbon-rich solid material produced from gas-phase precursors. Most of the unburned carbon in coal fly ash results from the unburned char, as soot is assumed to make a negligible contribution to carbon in the ash because its particles are less reactive than char (Hurt and Gibbins, 1995; Veranth et al., 1998).

The amount of unburned carbon in fly ash is partially contributed to the loss in mass when LOI test is performed. The LOI test is the standard method used to determine the mass loss in fly ash, in which a sample of fly ash is dried and weighed before being placed in an ashing furnace for several hours at 750°C. The sample is then reweighed and the loss in weight is obtained (ASTM, 2009). Loss on ignition can also be measured using Thermogravimetric Analysis (TGA). In TGA test, a small sample (50mg) of fly ash is dried for five hours at 150°C and stored in a sealed container until testing. At the time of analysis, the sample is placed in an alumina cup within the TGA chamber (the gas pressure is maintained positive with a throughput of 100 ml/min). During the first 30 min of the test, the sample is held at 25°C in a nitrogen gas flow to stabilize the weight of the sample. The heat is then raised at a constant rate of 20°C per min until the sample reaches 725°C (or to the required temperature) at which the gas flow is automatically switched from nitrogen to air. Changes in the weight of the sample, during the test, are recorded as a function of both time and temperature. In TGA oxidising atmosphere, the loss on ignition in fly ash is not only because of the oxidation process of unburned carbon, but also due to the decomposition of other compounds. This includes the decomposition of calcium hydroxide (400-450C), carbonate decomposition (650-750°C) and the mass loss due to removal of hydroxyl groups (450-750°C), as shown in Figure 2.35. In an inert atmosphere (e.g. nitrogen gas) when a sample is heated to 750°C all chemical reactions take place, except carbon oxidation. Above 750°C, TGA changes nitrogen to air and the carbon is then oxidised. The loss in mass then represents the carbon content (Brown and Dykstra, 1995; Paya et al., 2002).

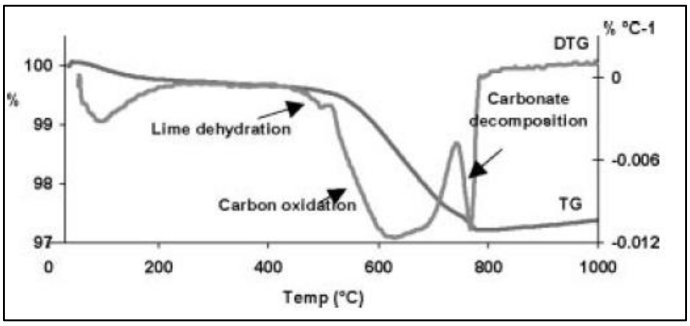


Figure 2.35: TGA oxidising atmosphere (Paya et al., 2002).

A comparative study was carried out by Brown and Dykstra (1995) to identify the accuracy of both LOI and TGA test in determining the amount of mass loss in seven different fly ashes. The study concluded that the cumulative weight losses for LOI and TGA agreed to within 2%.

The existing beneficiation methods of removing unburned carbon from fly ash mainly rely on applying physical processes. These methods involve combustion, separation, dry or wet electrostatic, air classifications, vibratory method, forth floatation and sieving. Although there is currently a wide variety of techniques used to remove carbon, most suffer from disadvantages. Most of physical separation methods cannot fully remove unburned carbon, whilst the more efficient carbon separation and utilisation methods involve significant capital investment. Therefore, researchers have been working to investigate more effective treatment methods. This includes application of supercritical water oxidation, which involves heating water up to 374^{o}C under 218 atmospheres pressure. This process encourages heated water to react with carbon and hence produce carbon dioxide (Hamley et al., 2001). Additional technique includes the use of tribo parallel plate separator, which consists of a venturi feed system driven by nitrogen pressure, an injection nozzle, and a high voltage separation section (Figure 2.36). The fly ash particles are introduced via the venturi feeder and then charged by their contact with the copper tubing and with one another. As a result of this electrical charge, positively charged particles (carbon concentrates) and negatively charged particles (mineral concentrates) will form. The positively charged unburned carbon particles are attracted to the negative electrode and the negatively charged mineral particles are moved to the positive electrode (Gray et al., 2002).

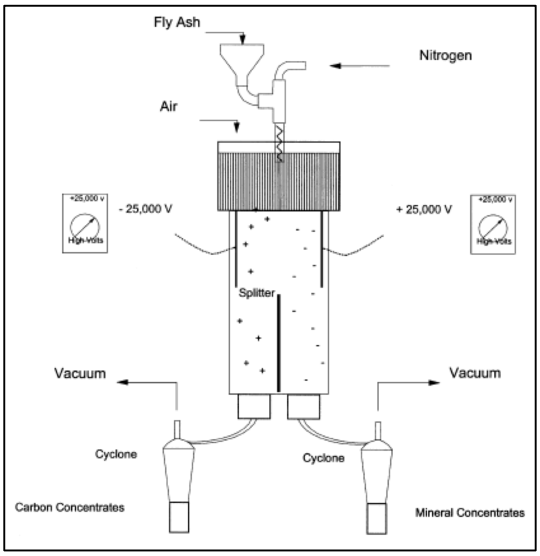


Figure 2.36: Schematic drawing of tribo electrostatic separator (Gray et al., 2002).

The utilisation of unprocessed fly ash in the construction applications was introduced. Jones and McCarthy (2005) investigated the influence of using unprocessed fly ash as a sand replacement in foamed concrete. Foamed concrete with plastic densities ranging between 1000 and 1400 kg/m^3 with cube strengths between 1 and 10 MPa were tested. It was shown that the incorporation of unprocessed fly ash significantly enhanced compressive strength development, with a noticeable improvement to sulphate attack. The presence of carbon significantly reduced the workability and therefore it was required to greatly increase the amount of foam to achieve the specified design plastic density.

Snelson and Kinuthia (2010a) carried out a study to examine the physical, mechanical and chemical characteristics of mortar mixes containing unprocessed fly ash as a cement replacement. Mortar specimens were cured for 28 days and were tested for their splitting tensile strength and sulphate attack resistance. The study showed good resistance to sulphate attack. The tensile splitting strength decreased when the amount of fly ash was increased. Compressive strength development of concrete specimens containing unprocessed fly ash and soaked in sulphate solution was investigated by Snelson and Kinuthia (2010b). The study concluded that concrete contained unprocessed fly ash did not show good early strength development. However, a noticeable improvement in compressive strength was observed at longer age.

Rejected fly ash is the portion of fly ash that is rejected from the ash classifying process due to its high carbon content and large particle size. A significant amount of fly ash is therefore accumulated and has remained unused, causing additional pressure on local authorities and environmental organizations. Rejected fly ash is not suitable for use in the construction due to its high carbon content and large particle size (>45 µm). However, rejected fly ash has the potential to be used in certain engineering applications, such as in solidification and stabilization processes of hazardous waste and materials for road base or subbase construction, which require relatively lower strength and reactivity (Poon et al., 2003).

Recent studies investigated the potential of utilising rejected fly ash in the construction industry to produce cement-based materials. Poon et al. (2003) studied the Pozzolanic properties of reject fly ash in blended cement pastes. Ordinary Portland Cement (OPC) with two class F fly ashes were used. The first fly ash was a classified fly ash passed through the 45-µm classifying process (f-FA); the other one was rejected fly ash (r-FA) with a particle size greater than 45 µm. The cement/fly ash mixes were prepared with the following proportions. Three mixes, for both the f-FA and r-FA, were prepared with fly ash to OPC ratios of 100:10, 100:25 & 100:40 and water to binder ratio of 0.28. One more mix with higher w/b of 0.35 was also prepared to investigate the influence of water content on the hydration process. A control mix without fly ash was prepared at the same w/b. Additionally, lime and other activators were added to test the effects of different activators on the hydration of r-FA. 40x80 mm in size cylindrical moulds were used. Cast samples were cured in a fog tank at 25°C until testing at 7, 28, and 90 days. Results showed that compressive strength decreases with increasing fly ash amount, and compressive strength for mixes incorporating f-FA was significantly higher than mixes with r-FA. However, compressive strength for r-FA mixes can be improved by including activation agents (Figure 2.37, Figure 2.38 and Figure 2.39). The strength development for mixes with higher w/b ratios was greater than that for mixes with lower w/b ratio: It seems that a higher but not excessive w/b benefited the hydration and strength development of the r-FA cement pastes.

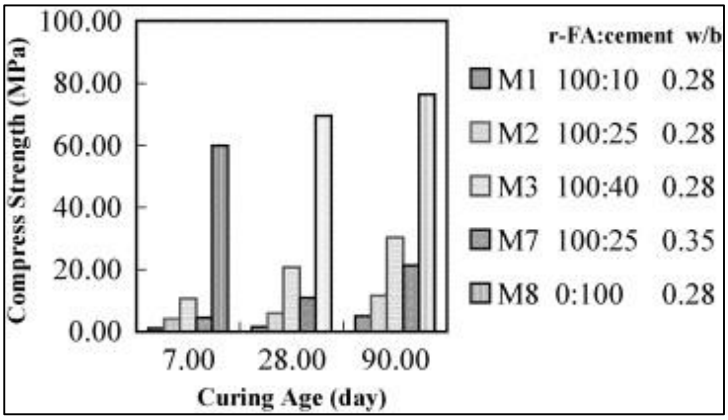


Figure 2.37: Compressive strength development of r-FA paste specimens (Poon et al., 2003).

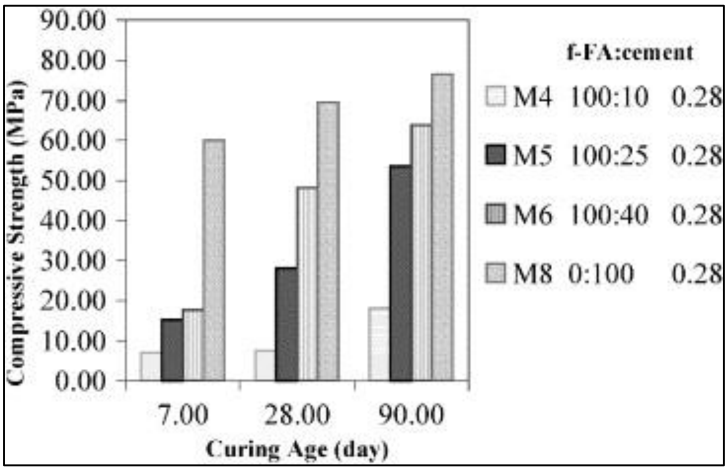


Figure 2.38: Compressive strength development of f-FA paste specimens (Poon et al., 2003).

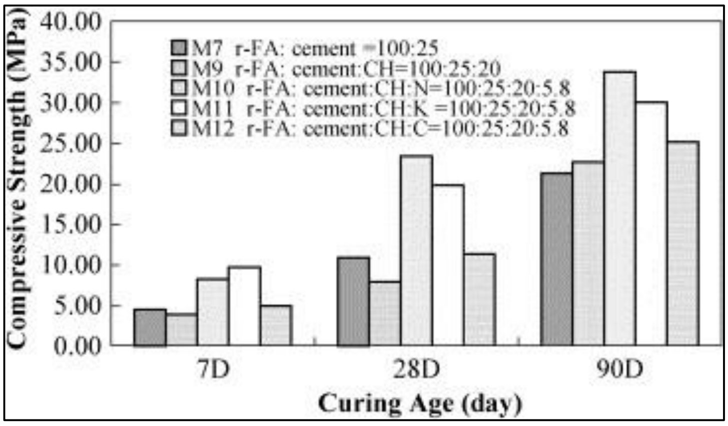


Figure 2.39: Compressive strength development of r-FA paste specimens with $Ca(OH)_2$ and chemical activators (note: CH–$Ca(OH)_2$, N–Na_2SO_4, K–K_2SO_4, and C–$CaCl_2$) (Poon et al., 2003).

2.4 SUMMARY AND RESEARCH GAP

The literature review showed that only fully or partially treated sewage sludge products have been used in the construction and civil engineering applications. Different forms of sewage sludge were investigated included dewatered sewage sludge (sludge cakes), thermally dry sewage sludge and Incinerated Sewage Sludge Ash (ISSA). Sewage sludge products were utilised in construction applications for the production of several building materials including ceramic tiles, ceramic products, and lightweight materials, as well as in other civil engineering applications such as soil stabilisation and wastewater treatment. Sewage sludge products were also included in cement-based materials as a treatment practice. ISSA was used as a full or partial replacement of the traditional raw materials used in mortar mixes, glass, ceramics, flooring tiles, lightweight construction materials, and lightweight aggregates. ISSA was also used in stabilising soil. Thermally dried sewage sludge was used in different construction applications including the production of ceramics and lightweight aggregate. The dewatered sewage sludge was used to manufacture lightweight aggregates, unfired bricks, cement paste, and mortar & concrete mixes.

It addition to the sewage sludge products, this chapter investigated the literature of utilising fly ash products in the construction industry, which confirmed that the inclusion of fly ash in cement-based materials positively contributes to the mechanical and durability properties. Positive contributions include improvement in long-term strength, reduction in hydration temperature, reduction in drying shrinkage and improvement in resisting sulphate attack. Although there is very limited information about the utilisation of rejected and unprocessed fly ashes, the literature suggested that the incorporation of these materials in cement-based mixes would also improve the mechanical and durability properties.

Based on the outcomes of this literature review, there was not any investigation recently undertaken to assess the possibility of utilising Raw Sewage Sludge (RSS) in construction applications. The literature review also did not reveal any substantial research that was carried out on construction materials containing a combination of RSS and unprocessed fly ash.

Since RSS contains about 97% water of total mass, it can be utilised as a water replacement in cement-based materials. Unprocessed fly ash can also be utilised as cement replacement due to its predicted positive contributions to the long-term strength development and sulphate resistance. It also predicted to positively contribute to the leaching properties by improving the immobility of pollutants in RSS due to the pores and absorbent nature of the unburned carbon that is present in the unprocessed fly ash. In order to bridge the identified gap, this research proposes the use of Raw Sewage Sludge (RSS) as a water replacement in cement-based materials incorporating unprocessed fly ash as cement replacement.

In addition to the production of sustainable construction materials, the outcome of this research could see huge financial savings to the current economical constraints by eliminating the costly processes involved in treating these wastes. This would also significantly reduce the energy consumption. Furthermore, there are huge environmental benefits from the avoidance of sending RSS to landfills and incinerators.

CHAPTER 3: EXPERIMENTAL METHODOLOGY

3.1 SCOPE

This chapter consists of three main sections; the first section provides detailed information about materials used throughout the experimental programme, as well as mixing proportions. The second section describes the procedures that were followed to prepare, mix, cast and cure specimens. The last section discusses the techniques and measuring procedures that were used to determine engineering, durability and environmental properties.

3.2 AIMS AND OBJECTIVES

The aim of this experimental programme was to introduce an effective alternative to the traditional treatment and re-use methods of both Raw Sewage Sludge (RSS) and unprocessed fly ash currently in place. Alternative include the utilisation of Raw Sewage Sludge (RSS) as a water replacement in cement-based materials containing unprocessed fly ash. The experimental programme investigated physical, mechanical, durability and environmental properties of mortar and concrete mixes contained RSS and unprocessed fly ash. The following characteristics were evaluated:

- Workability/flowability
- Density
- Total Water Absorption (TWA)
- Compressive strength
- Ultrasonic Pules Velocity (UPV)
- Flexural tests
- Length change
- Durability test (Sulphate attach resistance)
- Environmental test (Leaching test)

3.3 MATERIALS PROPERTIES

3.3.1 Introduction

Table 3.1 lists the materials that were used throughout the experimental programme, including Portland cement, fine aggregate (sand), coarse aggregate (gravel), drinking water, Raw Sewage Sludge (RSS) and unprocessed fly ash. Additional materials were also used for other applications. This included hydrated lime, deionised water and Sodium sulphate (Na_2SO_4).

Table 3.1: Application of used materials.

Material	Application
Portland cement	Main binding material
Fine aggregate (sand)	Aggregate for mortar and concrete mixes
Coarse aggregate (gravel)	Aggregate for concrete mixes
Water	For control mixes
Raw Sewage Sludge (RSS)	As a water replacement in mortar and concrete mixes
unprocessed fly ash	As a cement replacement in mortar and concrete mixes
Hydrated lime	To partially treat Raw Sewage Sludge (RSS)
Deionised water	Used for leaching test
Sodium sulphate (Na_2SO_4)	Used for sulphate attack resistance test

3.3.2 Portland cement

The cement used throughout the experimental programme was Portland Cement (PC) that complies with the requirements of BS EN 197-1:2000 type CEM I Portland cement strength class 42.5 (BSI, 2000a). The mineral composition of used cement is shown in Table 3.2.

Table 3.2: Mineralogical composition of cement

Compound	Oxide composition	% weight
Tricalcium Silicate (C_3S, alite)	$3CaO.SiO_2$	55.7
Dicalcium Silicate (C_2S, belite)	$2CaO.SiO_2$	17.8
Tricalcium Aluminate (C_3A)	$3CaO.Al_2O_3$	7.1
Tetracalcium Aluminoferrite (C_4AF)	$4CaO.Al_2O_3.Fe_2O_3$	8.5

3.3.3 Fly ash

The fly ash used in this experimental work was unprocessed fly ash that was collected from West Burton Power Station in the UK. The unprocessed fly as had a high loss on ignition value (23% of total weight at 100-850^oC), which was due to the high content of unburned carbon. Figure 3.1 shows the loss on ignition analysis using Thermogravimetry.

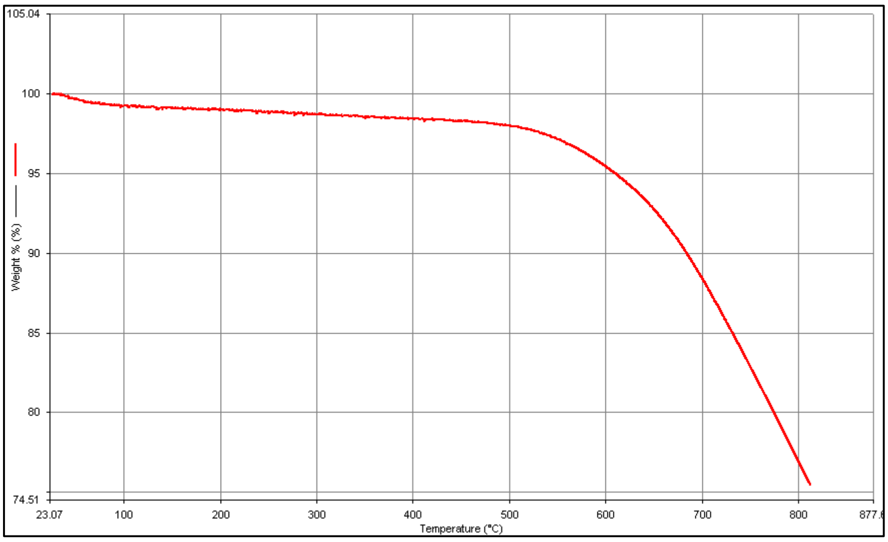


Figure 3.1: Thermogravimetry results for unprocessed fly ash.

A number of analytical tests were carried out on the unprocessed fly ash sample. These included moisture content, bulk density, particle density, and chemical analyses using X-Ray Fluorescence (XRF). The results are presented in Table 3.3. Magnified images of the unprocessed fly ash samples were obtained using Scanning Electron Microscopes (SEM) technology (Figure 3.2). The particle size distribution of the unprocessed fly ash sample is presented in Figure 3.3.

Table 3.3: Physical and chemical properties of unprocessed fly ash sample.

Property/element	Unit	Value	Techniques
Moisture content	% weight	0.78	-
Bulk density	(Kg/m^3)	442	BS EN 1097-3:1998 (BSI, 1998)
Dry particle density	(Kg/m^3)	1824	100ml Pycnometer
SiO_2	% tw	45.06	SPECTRO XEPOS-X-Ray Fluorescence (XRF)
Al_2O_3		16.94	
Fe_2O_3		9.04	
CaO		1.96	
K2O		1.4	
MgO		1.02	
TiO_2		0.71	
Na_2O		0.34	
P_2O_5		0.19	
BaO		0.08	
ZrO_2		0.07	
SrO		0.06	
MnO		0.05	
ZnO		0.04	
Cr_2O_3		0.02	
CuO		0.02	
PbO		0.02	
Loss on ingestion (LOI)	% tw	23	Thermogravimetry

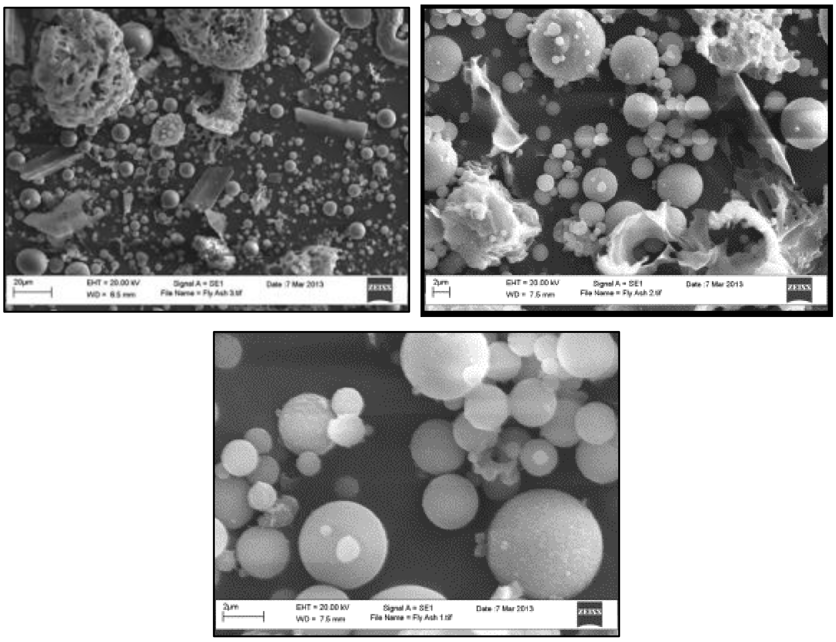


Figure 3.2: Images of unprocessed fly ash particles using Scanning Electron Microscopes (SEM).

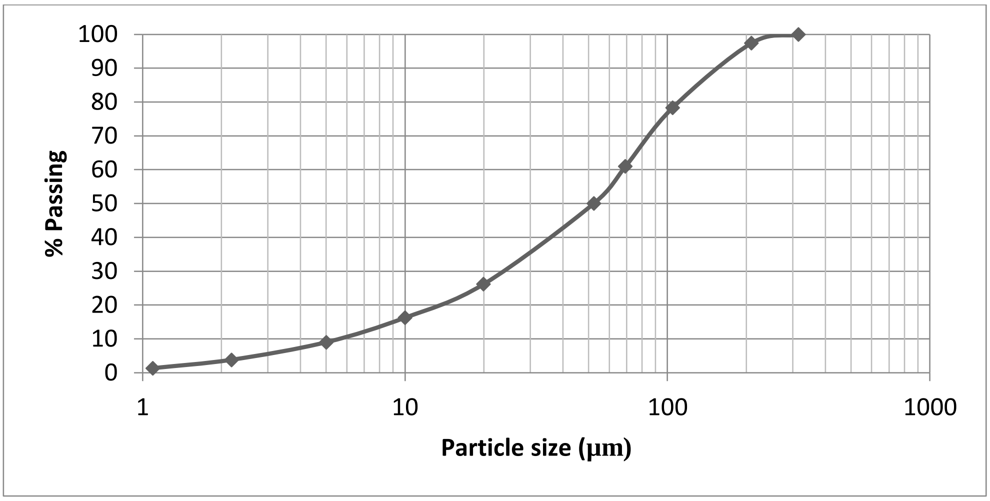


Figure 3.3: Particle size distribution of the unprocessed fly ash sample.

3.3.4 Aggregates

The sand used throughout the experimental programme was size 0/4 that complies with the requirements of BS EN 12620:2002+A1:2008 category G_F85 (BSI, 2008a), and fines content category 1 (BSI, 2002d), whereas the coarse aggregate was crushed stone size 4/20 that complies with the requirements of BS EN 12620:2002+A1:2008 category $G_C90/15$ (BSI, 2008a). Figure 3.4 shows the sieve analysis for both sand and coarse aggregates that was determined in accordance to BS EN 933-1:2012 (BSI, 2012c) and BS EN 933-2:1996 (BSI, 1996c). Table 3.4 presents the physical properties.

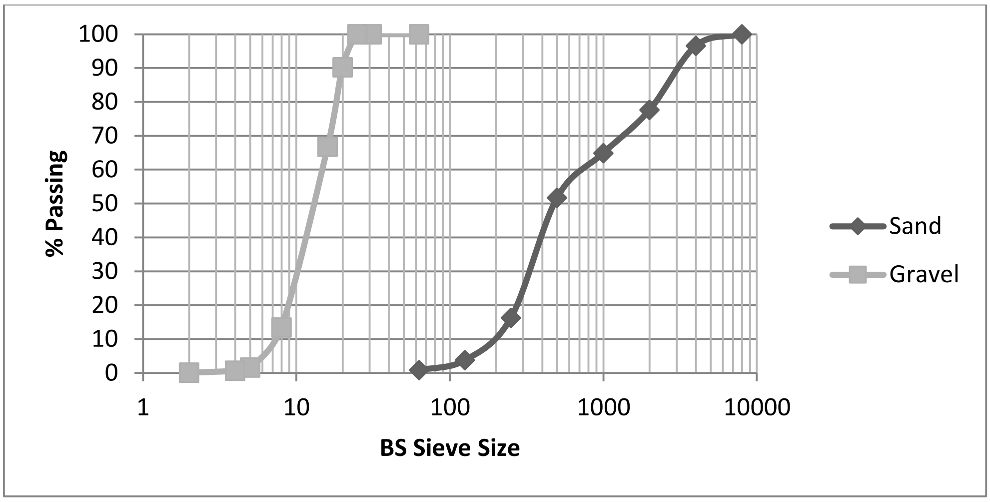


Figure 3.4: Particle size distribution of the sand and gravel.

Table 3.4: Physical properties of the fine and coarse aggregates.

Property	Fine aggregates (Sand)	Coarse aggregates (Gravel)	Standard
Loose bulk density (Kg/m^3)	1660	1570	BS EN 1097-3:1998 (BSI, 1998)
Specific Gravity (SSD)	2.65	2.59	BS EN 1097-6: 2000 (BSI, 2000c)
Water absorption-saturated and surface-dry condition (SSD)(% weight)	1.1	1.1	BS EN 1097-6: 2000 (BSI, 2000c)

3.3.5 Mixing Water

The water used throughout the experimental programme was drinking water supplied by Severn Trent company that complies with the requirements of BS EN 1008:2002 (BSI, 2002a) and BS EN 206-1:2000 (BSI, 2000b).

3.3.6 Raw Sewage Sludge (RSS)

Raw Sewage Sludge sample was collected from a Sewage Treatment Works in the West Midlands in the form of thick slurry that contains 97.5% total weight liquid (Figure 3.5). 0.5% total weight hydrated lime was added to the Raw Sewage Sludge for partial treatment. Hydrated lime was added to increase alkalinity level (pH>12) to eliminate hazardous pathogens as seen in Figure 3.6. The amount of hydrated lime added was estimated based on recommendations made by the British Lime Association (British Lime Association, 2013).

Figure 3.5: Raw Sewage Sludge sample.

Figure 3.6: Raw Sewage Sludge pH check.

Collected Raw Sewage Sludge (RSS) sample was later emptied into smaller containers (2.5 litre containers) and placed in a freezer. Raw Sewage Sludge sample was frozen for health and safety reasons, and to prevent possible changes in properties that could occur as a result of biological degradation process (Figure 3.7 and Figure 3.8).

Figure 3.7: Raw Sewage Sludge sample in small containers.

Figure 3.8: Freezing Raw Sewage Sludge samples.

A number of analytical tests were carried out on Raw Sewage Sludge sample. These included water content, density, heavy metal content, and free ions. The results are presented in Table 3.5. Further tests were carried out on dry sewage sludge including X-Ray Fluorescence (XRF) and loss on ignition (Thermogravimetry) tests. The results are shown in Table 3.6 and Figure 3.9.

Table 3.5: Raw Sewage Sludge properties.

Property/material	Unit	Value	Techniques
Unit weight	Kg/m^3	1012	100ml Pycnometer
Solid content	% weight	2.5	-
Chloride Nitrate Phosphate Sulphate	ppm	32.19 2.94 1.38 23.93	ICS-90A-Ion Chromatography System (Section 3.5.11)
Cr Cu Ni Sn Zn Mn Fe Al As Ba S P Na Mg K Ca	ppm	1.19 5.33 2.51 0.04 19.08 3.92 147.72 77.83 0.27 7.55 65.22 200.83 199.65 54.77 121.05 33793.35	Inductively coupled plasma using SPECTRO $CIROS^{CCD}$ ICP (Section 3.5.11)

Table 3.6: Chemical composition of dry solids of sewage sludge using X-Ray Fluorescence (XRF).

Element	Value (%wt)	Oxides	Value (%wt)
Na	17.4	Na_2O	23.46
Mg	2.02	MgO	3.35
Al	1.34	Al_2O_3	2.53
Si	3.99	SiO_2	8.54
P	3.51	P_2O_5	8.04
S	1.78	SO_3	4.45
Cl	0.15	Cl	0.15
K	0.48	K_2O	0.58
Ca	24.14	CaO	33.78
Ti	0.24	TiO_2	0.4
Fe	7.77	Fe_2O_3	11.11
Zn	0.21	ZnO	0.26

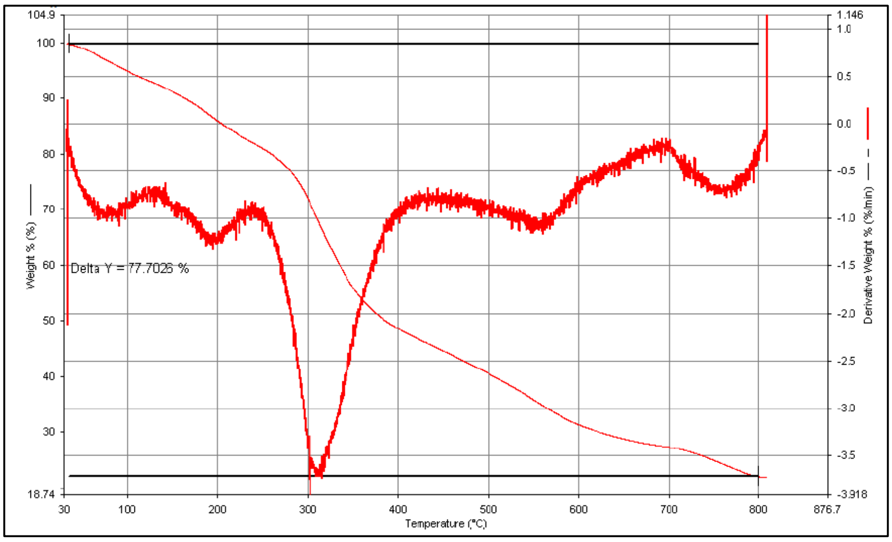


Figure 3.9: Thermogravimetry results for dry sewage sludge.

3.3.7 Deionised water

Deionised water was used for obtaining samples for leaching tests. Deionised water was used as an immersion medium for mortar and concrete samples for the leaching test analysis.

3.3.8 Hydrated lime

Hydrated lime that complies with BS EN 459-1: 2010 (BSI, 2010a) was used to partially treat Raw Sewage Sludge (RSS). 0.5% total weight of hydrated lime was added to the RSS sample to eliminate hazardous pathogens by raising pH above 12. The amount of hydrated lime added was estimated based on recommendations made by the British Lime Association (British Lime Association, 2013).

3.3.9 Sodium Sulphate

Sodium sulphate (Na_2SO_4) was used throughout the experimental programme for sulphate attack resistance test. 5% total weight of sodium sulphate was mixed with water (50g of Na_2SO_4 to 950g of water) to form the sulphate solution that was required for carrying out the sulphate attack resistance test.

3.3.10 Mixing Proportions

Three series of cement-based mixes were investigated throughout this experimental programme. These included mortar mixes with RSS and unprocessed fly ash, mortar mixes with RSS and large proportions of unprocessed fly ash, and concrete mixes with RSS and unprocessed fly ash.

Series 1 *(Mortar mixes with RSS and unprocessed fly ash)* consisted of 17 mixes mainly contained a constant sand to binder ratio of 4.5 (by mass) with different liquid to binder ratios (0.5, 0.65, 0.8 and 1). Unprocessed fly ash was used as a cement replacement at four ratios of 0, 10, 20 and 30% by mass of total binder. Mixing ratios were considered based on the literature review, a number of trial mixes and some practical guidance. The main sand to cement ratio of 4.5 was decided based on practical guidelines (BSI, 2003a). However, other sand to cement ratios, including 3, 6 and 7.5, were also investigated. The percentages of unprocessed fly ash were decided based on the outcome of the literature review. The liquid content (Liquid/Binder ratio) was considered to be ranged from 0.5 to 1 in order to produce workable mixes (the lower limit), and to avoid mixes segregation during casting (the upper limit). The mixing proportion of this series is presented in Table 3.7. This series was divided into five different groups and as shown in Table 3.8.

A brief summary about each group is as follows:

- Group 1: the main objective of this group was to examine the influence of varying RSS content on the investigated properties. One sand to cement ratio of 4.5 and four RSS/Cement ratios of 0.5, 0.65, 0.8 and 1 were used.
- Group 2: this group was designed to assess the impact of varying sand content on the investigated properties. One RSS/Cement ratio of 0.8 and four sand to cement ratios of 3, 4.5, 6 and 7.5 were used.

- Group 3: this group was designed to evaluate the impact of partially replacing cement with unprocessed fly ash on tested properties. Cement was replaced with unprocessed fly ash at four ratios of 0, 10, 20 and 30% by weight of total binder. The RSS/Binder ratio in this group was 0.65.
- Group 4: similar to group 3, but with a higher RSS/Binder ratio (0.8).
- Group 5: the composition of this group was similar to group 4, but with water. This group was considered as the control and the results were compared with Group 4.

Table 3.7: Mixing proportions for mortar mixes with RSS and unprocessed fly ash (Series 1).

Mix	Liquid/Binder	Binder		Sand to binder ratio	Liquid type
		Cement	Fly ash		
M1	0.5	1	0	4.5	RSS
M2	0.65	1	0	4.5	RSS
M3	0.8	1	0	4.5	RSS
M4	1	1	0	4.5	RSS
M5	0.8	1	0	3	RSS
M6	0.8	1	0	6	RSS
M7	0.8	1	0	7.5	RSS
M8	0.8	0.9	0.1	4.5	RSS
M9	0.8	0.8	0.2	4.5	RSS
M10	0.8	0.7	0.3	4.5	RSS
M11	0.65	0.9	0.1	4.5	RSS
M12	0.65	0.8	0.2	4.5	RSS
M13	0.65	0.7	0.3	4.5	RSS
M14	0.8	1	0	4.5	Water
M15	0.8	0.9	0.1	4.5	Water
M16	0.8	0.8	0.2	4.5	Water
M17	0.8	0.7	0.3	4.5	Water

Table 3.8: Mix groups and investigated properties for Series 1.

Group	Mix	Investigated properties
1	M1, M2, M3 and M4	Flowability, density, Total Water Absorption (TWA), Ultrasonic Pulse Velocity (UPV), compressive strength, flexural strength, drying shrinkage, sulphate attack and leaching test
2	M5, M3, M6 and M7	Flowability, density, Total Water Absorption (TWA), Ultrasonic Pulse Velocity (UPV), compressive strength and leaching test
3	M2, M11, M12 and M13	Flowability, density, Total Water Absorption (TWA), Ultrasonic Pulse Velocity (UPV), compressive strength, flexural strength, drying shrinkage, sulphate attack and leaching test
4	M3, M8, M9 and M19	Flowability, density, Total Water Absorption (TWA), Ultrasonic Pulse Velocity (UPV), compressive strength, flexural strength, drying shrinkage, sulphate attack and leaching test
5	M14, M15, M16 and M17	Flowability, density, Total Water Absorption (TWA), Ultrasonic Pulse Velocity (UPV), compressive strength, flexural test, drying shrinkage, sulphate attack and leaching test

Series 2 ***(Mortar mixes with RSS and large proportions of unprocessed fly ash)*** consisted of five mixes that incorporated a constant sand to binder ratio of 4.5 (by mass) with a liquid to binder ratio of 1. Cement was replaced with 0, 40, 60 and 80% unprocessed fly ash by mass of total binder. This series also included the control mix, which was made with water and 0% unprocessed fly ash. The main objective of this series was to investigate the influence of including large proportions of unprocessed fly ash on tested properties. Liquid/Binder ratio of 1 was considered to produce mortar mixes with reasonable workability as the inclusion of unprocessed fly ash significantly reduces workability (based on trial mixes). Table 3.9 shows the mix proportions of this series.

Table 3.9: Mixing proportions for mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2).

Mix	Liquid/Binder	Binder		Sand	Liquid type	Investigated properties
		Cement	Fly ash			
ML1	1	1	0	4.5	RSS	Flowability, density, Total Water Absorption (TWA), Ultrasonic Pulse Velocity (UPV) and compressive strength
ML2	1	0.6	0.4	4.5	RSS	
ML3	1	0.4	0.6	4.5	RSS	
ML4	1	0.2	0.8	4.5	RSS	
MLRef	1	1	0	4.5	Water	

Series 3 ***(Concrete mixes with RSS and unprocessed fly ash)*** consisted of five mixes that incorporated a constant cement:sand:gravel ratio of 1:1.5:3 respectively (by mass) and a constant liquid to binder ratio of 0.5. Cement was replaced with 0, 10, 15, 20% unprocessed fly ash by mass of total binder. This series included the control mix, which was made of drinking water and 0% unprocessed fly ash. This series was designed based on the initial results of Series 1. The aggregate (sand and gravel) ratio was maintained at 4.5 by mass and

the maximum content of unprocessed fly ash was limited to 20% of total binder weight (the best compressive strength of Series 1 was achieved at this ratio). Table 3.10 presents the mix proportions of this series.

Table 3.10: Mixing proportion for concrete mixes with RSS and unprocessed fly ash (Series 3).

Mix	Liquid/Binder	Binder C:FA		Sand	Gravel	Liquid type	Investigated properties
		Cement	Fly ash				
CM1	0.5	1	0	1.5	3	RSS	Workability, density, Total Water Absorption (TWA), Ultrasonic Pulse Velocity (UPV), compressive strength, flexural strength, drying shrinkage and sulphate attack
CM2	0.5	0.9	0.1	1.5	3	RSS	
CM3	0.5	0.85	0.15	1.5	3	RSS	
CM4	0.5	0.8	0.2	1.5	3	RSS	
CMRef	0.5	1	0	1.5	3	Water	

3.4 PREPARATION, MIXING AND CASTING

3.4.1 Preparation

The aggregate and unprocessed fly ash samples were dried in an electrical oven at 100^{o}C for 24 hours; thereafter dried samples were cooled down at a room temperature for 2 hours. Frozen RSS was placed in a room temperature for 48 hours to defrost completely and to thermally neutralise.

3.4.2 Mixing

The dry components of mortar mixes, with or without unprocessed fly ash, were mixed manually until homogeneity was achieved; thereafter mixing liquid (RSS or water) was added and mixed. Additional liquid, 1.1% total weight sand, was added to compensate for water absorption requirements for dry sand to achieve Saturated Surface-Dry (SSD) conditions.

Concrete mixtures were mixed in accordance to BS 1881-125:1986 (BSI, 1986) using ELE mechanical mixer until homogeneity was achieved (Figure 3.10). Additional liquid, 1.1% total weight aggregate, was added to compensate for water absorption requirements for dry aggregate to achieve SSD condition.

Figure 3.10: ELE mechanical mixer for concrete mixes.

3.4.3 Casting

Steel moulds (50mm in size) were used to cast the mortar specimens for the determination of compressive strength, density, Ultrasonic Pulse Velocity (UPV), Total Water Absorption (TWA), sulphate attack and leaching test. Mortar samples were prepared in accordance to ASTM C109/C109M-02 (ASTM, 2008). For concrete mixes, 100mm in size steel moulds were used to cast the samples for the determination of compressive strength, density, Ultrasonic Pulse Velocity (UPV), Total Water Absorption (TWA) and sulphate attack. Concrete cubes were prepared in accordance to BS 1881-125:1986 (BSI, 1986), and were compacted using a mechanical vibrator. Figure 3.11 shows the steel moulds that were used throughout the experimental programme.

A: 50mm in size steel moulds B: 100mm in size steel mould

Figure 3.11: Cubic steel moulds used throughout the experimental programme.

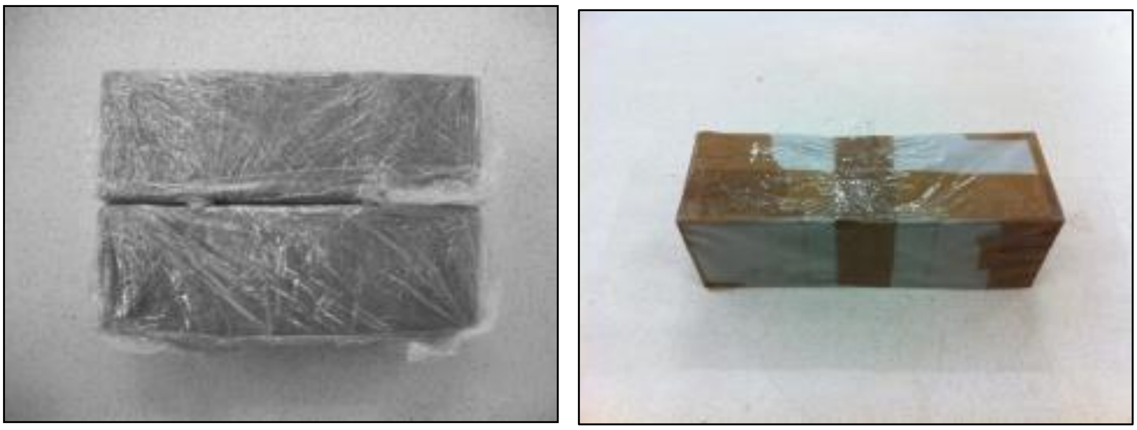
Steel prisms (40x40x160mm in size) that comply with BS EN 196-1:2005 (BSI, 2005) and BS EN 12617-4:2002 (BSI, 2002b) were used to cast mortar samples for the determination of flexural strength and drying shrinkage. Mortar prisms were cast manually in three layers, each of which received 32 uniform strokes. For concrete mixes, steel prisms (75x75x400mm in size) that comply with BS ISO 1920-8:2009 (BSI, 2009f) were used to ascertain drying shrinkage. 100x100x500mm in size steel mould was used to prepare concrete samples for flexural tests. Concrete prisms were prepared according to BS 1881-125:1986 (BSI, 1986), and were compacted using a mechanical vibrator. Figure 3.12 shows the steel prisms that were used throughout the experimental programme.

A: 40x40x160mm B: 75x75x400mm C: 100x100x500mm

Figure 3.12: Steel prisms used throughout the experimental programme.

3.4.4 Curing

After casting, specimens were covered with plastic sheets and placed in a room at a temperature of 20±2°C for 24 hours until demoulding. Thereafter, specimens were cured for different ages (between 1 and 365 days) by wrapping them with sealed cling film (for mortar samples) or by plastic sheets (for concrete samples). Tank curing was avoided in order to minimize any potential pollution. Specimens in Series 1 were cured for 1, 7, 28, 90 and 365 days. Series 2 was cured for 1, 7, 28, 90 and 180 days, whereas Series 3 was cured for 1, 7, 28, 90 and 300 days. Series 2 and 3 were cured for less than 365 days due to time restrains. Figure 3.13 shows the curing system that was applied throughout the experimental work.



A: mortar samples B: concrete samples

Figure 3.13: Curing system for mortar and concrete specimens.

3.5 TESTING

3.5.1 Flowability/Workability

Flow table that complies with BS EN 1015-3:1999 (BSI, 1999a) was used to obtain the flowability for mortar mixes. The mould was centrally placed on the disc of flow table, and mortar was introduced in two layers, each layer was compacted at least 10 times using a tamper to ensure uniform filling of the mould. After approximately 15 seconds, the mould was vertically raised, and the fresh sample was spread out on the disk by jolting the flow table 15 times at a constant frequency of approximately one per second. The diameter of the mortar was measured in two directions at right angles to one another using callipers. The results were recorded to the nearest mm. Figure 3.14 shows the flow table apparatus.

Figure 3.14: Flow table for mortar mixes.

Workability for concrete samples was obtained using slump test that complies with the requirements of BS EN 12350-2:2009 (BSI, 2009a). A steel hollow mould (200 ± 2 mm base diameter, 100 ± 2 mm top diameter and 300 ± 2mm height) was used. The mould was filled with fresh concrete in three consecutive layers, each approximately one-third of the height. Each layer received 25 strokes distributed uniformly over the cross-section, using a circular cross-section steel rod having a diameter of (16 ± 1) mm and length of (600 ± 5) mm. After removing the spilled concrete from the base plate, the mould was lifted steadily upwards with no lateral motion being imparted to the concrete. Immediately after removal of the mould, the difference between the height of the mould and that of the highest point of the slumped test specimen was recorded to the nearest 10 mm. Figure 3.15 shows slump test apparatus.

Figure 3.15: Slump test apparatus for concrete

3.5.2 Density

For the mortar specimen, mass of cured samples was measured using a sensitive scale with precision of 0.01g. The volume was obtained manually by measuring the specimen dimensions using an accurate calibre. Density was calculated using Equation 3.1, and the average density of three specimens was recorded to the nearest 1 Kg/m^3.

For the concrete specimens, mass of concrete specimens was recorded to the nearest 0.01Kg and the volume was obtained using water displacement method described in BS EN 12390-7:2009 (BSI, 2009d) as shown in Figure 3.16. Density was calculated using Equation 3.1, and the average of two specimens was recorded to the nearest 1 Kg/m^3. The volume of concrete samples was obtained using Equation 3.2.

Figure 3.16: Volume by water displacement method.

$$D = M/V \qquad Equation\ 3.1$$

<u>*Where*</u>

D is density in Kg/m^3;

M is mass of the specimen in Kg;

V is specimen volume in m^3.

$$V = \frac{m_{a} - ((m_{st}+m_{w}) - m_{st})}{P_{w}} \qquad Equation\ 3.2$$

<u>*Where:*</u>

V is the volume of the concrete specimen, in m^3;

ma is the mass of the specimen in air, in kg;

mst is the mass of holding stirrup/mesh in water, in kg;

mw is the mass of specimen in water, in kg;

P_w is the density of water, at 20°C, taken as 998 kg/m^3.

3.5.3 Total Water Absorption (TWA)

50x50x50mm in size specimens were used for mortar mixes, whereas 50x100x100mm in size specimens were used for concrete samples. Cured specimens were dried in an electrical oven at 75^{o}C until a constant weight. High drying temperature was avoided in order not to cause any damages to the test specimens. Thereafter, dried specimens were placed at a room temperature for two hours to cool down, and mass was later measured and recorded to the nearest 0.1g. Dried samples were immersed in drinking water until a constant weight (weight was monitor at different times). Prior to measuring mass of saturated samples, external surfaces were manually dried using damp towels. Total water absorption was calculated using Equation 3.3, and was recorded to the nearest 0.01% (the average of three mortar specimen and two concrete specimens).

$$TWA = \frac{m_S - m_d}{m_d} * 100\% \qquad Equation\ 3.3$$

<u>*Where*</u>

TWA is total water absorption %;

m_s is mass of saturated samples, in g;

m_d is mass of dried samples, in g.

3.5.4 Ultrasonic Pulse Velocity (UPV)

50x50x50 mm in size specimens were used for mortar mixes, whereas 100x100x100mm in size specimens were used for concrete samples. Ultrasonic pulse velocity is a traditional method used to examine quality of construction materials, mainly concrete, by measuring the time requirements for an ultrasonic pulse to transmit through tested specimens. Prior to crushing the specimens for compressive strength test, ultrasonic pulse velocity was obtained using Proceq Pundit Lab+ instrument (Figure 3.17). Ultrasonic pulse velocity was calculated using Equation 3.4, and was recorded to the nearest 1m/sec (the average of three mortar specimen and two concrete specimens).

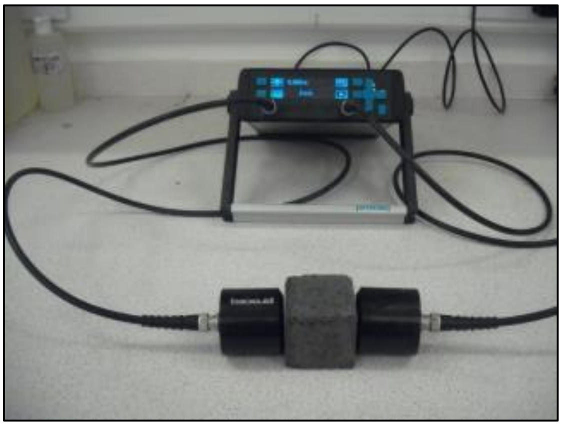


Figure 3.17: Proceq Pundit Lab+ ultrasonic pulse velocity instrument.

$$UPV = L/T \qquad Equation\ 3.4$$

Where

UPV is the ultrasonic pulse velocity, in m/sec;

L is the sample thickness, through which the ultrasonic pulse transmits, in m (0.05m for mortar specimens and 0.1m for concrete specimens);

T is the time required for the ultrasonic pulse to transmit through tested specimen, in sec.

3.5.5 Compressive Strength

For the mortar samples, the average compressive strength of three cubes was recorded to the nearest 0.1 MPa. Mortar samples were tested in accordance to ASTM C109/C109M-08 (ASTM, 2008) using SERCOMP7 hydraulic compressive strength machine with a loading rate of 2400 N/sec. For concrete mixes, cast cubes were tested in accordance to BS EN 12390-3:2009 (BSI, 2009b), with a loading rate of 0.6 MPa/sec. The average compressive strength of two specimens was recorded to the nearest 0.1 MPa. Figure 3.18 shows the compressive strength machine. The compressive strength was obtained using Equation 3.5.

Figure 3.18: SERCOMP7 hydraulic compressive strength machine.

$$fc = \frac{F}{A} \qquad \text{Equation 3.5}$$

<u>*Where*</u>

fc is the compressive strength, in MPa (N/mm^2);

F is the maximum load at failure, in N;

A is the cross-sectional area of the specimen on which the compressive force acts, in mm^2.

3.5.6 Flexural Strength

For the mortar mixes, 40x40x160 mm in size prisms that comply with BS EN 1015-11:1999 (BSI, 1999b) were used to obtain flexural strength. Figure 3.19 presents the dimension requirements for flexural test. Flexural strength was obtained using SERCOMP7 hydraulic compressive strength machine with loading rate of 50 N/sec. The average flexural strength of three prisms was calculated using Equation 3.6, and was recorded to the nearest MPa.

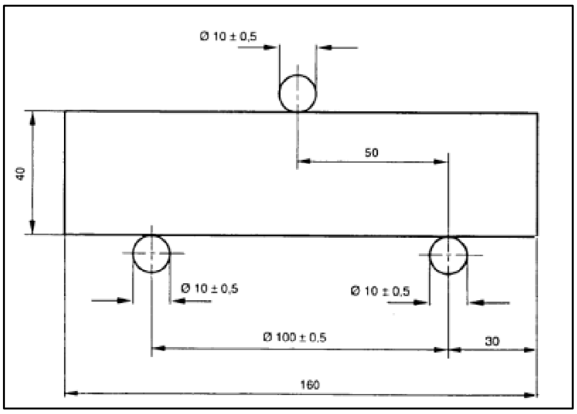


Figure 3.19: Flexural test requirements for mortar samples (BSI, 1999b).

For the concrete mixes, 100x100x500 mm in size prisms that comply with BS EN 12390-5:2009 (BSI, 2009c) were used for the determination of flexural strength. Figure 3.20 shows the standard requirements for flexural test. Flexural strength was obtained using SERCOMP7 hydraulic compressive strength machine with loading rate of 50 N/sec. The average flexural strength of two prisms was calculated using Equation 3.6, and was recorded to the nearest 0.1 MPa.

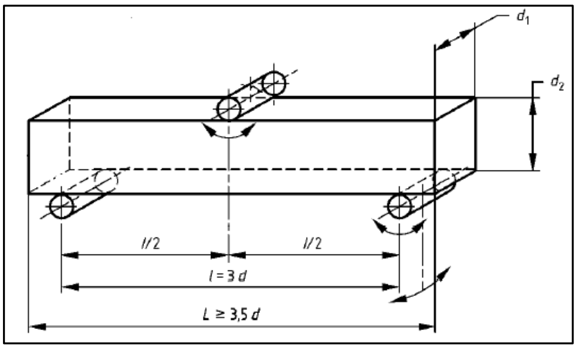


Figure 3.20: Flexural test requirements for concrete samples (BSI, 2009c).

$$f = 1.5\,\frac{Fl}{d_1 d_2^2} \qquad \text{Equation 3.6}$$

<u>*Where*</u>

f is the flexural strength, in MPa (N/mm²);

F is the maximum load at failure, in N;

l is the distance between the supporting rollers, in mm;

d_1 and d_2 are the lateral dimensions of the cross-section, in mm.

3.5.7 Length Change

Length change due to drying shrinkage for 40x40x160 mm in size mortar prisms was obtained. Two pairs of demec-studs were attached, at a distance of 100mm from each other, to the two sides of the prism that have been cast against the steel mould (Figure 3.21). Demec-studs were attached immediately after demoulding using super glue. Prisms were placed in a room at a temperature of 20°C ±2°C and a relative humidity of 50% ± 10%. Length change was monitored on a regular time intervals using a digital dial gauge. The average reading of three specimens (6 sides) was recorded to the nearest 1µstrain.

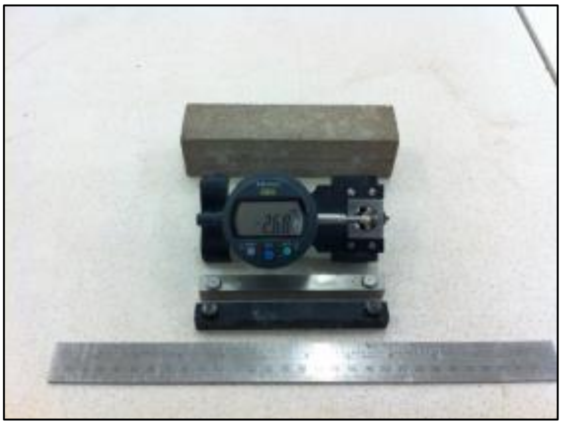


Figure 3.21: Length change due to drying shrinkage for mortar mixes.

For the concrete mixes, length change due to drying shrinkage was obtained using 75x75x280mm in size prisms that comply with the requirements of BS ISO 1920-8:2009 (BSI, 2009f). Two pairs of demec-studs were attached, at a distance of 100mm from one another, to the two sides of the prism that have been cast against the steel mould. Demec-studs were attached immediately after demoulding using super glue. Prisms were placed in a room at a temperature of 20°C ± 2°C and a relative humidity of 50% ± 10%. Length change was monitored at regular time intervals using a digital dial gauge (Figure 3.22). The average reading of two specimens (4 sides) was recorded to the nearest 1µstrain. For both mortar and concrete specimens, length change was obtained using Equation 3.7.

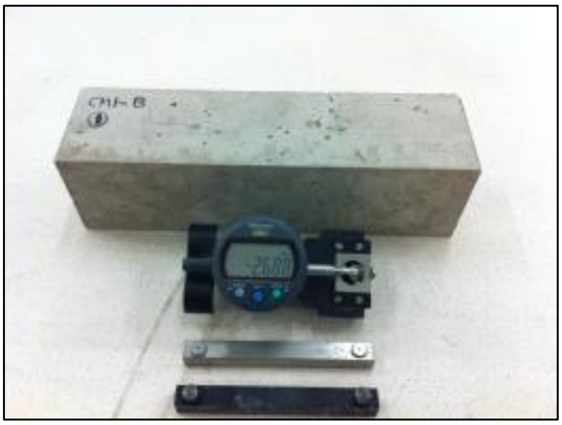


Figure 3.22: Length change due to drying shrinkage for concrete specimens.

$$\varepsilon = \frac{L_2 - L_1}{L_1} * 10^6 \qquad Equation\ 3.7$$

<u>*Where*</u>

ε is strain, in Mega Strain;

L2 is new length (new gauge reading), in mm;

L1 is the original length (original gauge reading), in mm.

3.5.8 Sulphate Attack

Mortar and concrete specimens were cured for 28 days and were immersed in a sulphate solution that was prepared in accordance to PD CEN/TR 15697:2008 (BSI, 2008c). The sulphate solution was prepared by mixing 5% (by weight) sodium sulphate (Na_2SO_4) with 95% (by weight) drinking water. Sulphate attack was evaluated by measuring changes in weight, compressive strength and visual observation during approximately 365 days of continuous exposure to sulphate solution. PH level was not monitored and sulphate solution was not changed throughout the course of the test.

18 mortar specimens (50x50x50mm in size) were used for each mix, 15 of which were placed in the sulphate solution immediately after the end of the curing (Figure 3.23). The remaining 3 were tested without being subjected to sulphate attack and were considered as the reference. Immersed specimens were tested (3 at a time) at various time intervals, subject to the deterioration levels.

For concrete mixes, 12 concrete specimens (100x100x100mm in size) were used for each mix, 10 of which were immersed in sulphate solution immediately after the end of the curing. The remaining 2 were tested without being subjected to sulphate attack and were considered as the reference. Immersed specimens were tested (2 at a time) at various time intervals, subject to the deterioration level.

For mortar mixes, the average compressive strength of three cubes (50 mm in size) was recorded to the nearest 0.1 N/mm^2. Mortar samples were tested in accordance to ASTM C109/C109M-08 (ASTM, 2008) using SERCOMP7 hydraulic compressive strength machine with a loading rate of 2400 N/sec. For concrete samples, the average compressive strength of two cubes (100 mm in size) was recorded to the nearest 0.1 N/mm^2. Concrete cubes were tested in accordance to BS EN 12390-3:2009 (BSI, 2009b), with a loading rate of 0.6 MPa/sec.

Figure 3.23: Mortar specimens immersed in sulphate solution.

3.5.9 Leaching Test

Two mortar specimens (50x50x50 mm in size) were cured for 28 days and used to perform leaching test. The leaching properties were obtained following test procedures described in Draft BS EN 15863:2008 (BSI, 2008b) . A brief description about the test procedures is as follows:

- The geometric surface area was determined, by measuring the length, width and height of the test specimen. Area was recorded in cm^2
- The leachant volume (the volume of water that was required to immerse test specimens) was calculated using Equation 3.8;

  $$V = (8 \pm 0{,}1) * A \qquad Equation\ 3.8$$

  <u>*Where:*</u>

  V is the volume of the leachant, in ml;

  A is the surface area of the test portion, in cm^2.

- Test specimens were placed in a plastic container using 2cm in height spacers, in order to prevent the test specimens from touching the inner side of the leaching container. Test specimens were placed in such a way that the minimum distance between the test specimens and the walls of the container was 2cm, all around;
- The plastic container with the test specimens was filled with the calculated volume (V) of deionised water in such a way that the top of the test specimens is at least 2cm submerged (below water level). The plastic container was closed to eliminate evaporation;
- The leaching process was allowed for 2 hours before eluate samples (water sample) were taken. Eluate samples were stored in 15ml plastic bottles and were frozen until being analysed;
- After obtaining the 2 hours immersion eluate, the plastic container was emptied and filled with fresh volume (V) of deionised water. The leaching process was allowed for 8 more days (8 days + 2 hours from the starting time). New eluate samples were taken, stored in 15ml plastic bottles and frozen until being analysed;
- After obtaining the 8 days immersion eluate, the plastic container was emptied and filled with fresh volume (V) of deionised water. The leaching process was allowed for 20 more days (28 days + 2 hours from the starting time). New eluate samples were taken, stored in 15ml plastic bottles and frozen until being analysed;
- Eluate samples were taken at three immersion times, 2 hours, 8 days and 28 days (Table 3.11).
- Eluate samples were analysed using Ion Chromatography System (IC) and Inductively Coupled Plasma (ICP).

Table 3.11: Leaching test immersion frequency.

Immersion frequency	Total immersion time
2 hours	2 hours
8 days	8 days + 2 hours
20 days	28 days+2 hours

3.5.10 Analytical Tests

A number of analytical tests were performed to determine various chemical, physical and environmental properties. Properties included obtaining the chemical composition of the materials used throughout the experimental programme (RSS and unprocessed fly ash), determining the concentration of pollutants when leaching test was performed, obtaining loss on ignition (for RSS and unprocessed fly ash), and finally taking magnified images. A brief summary about the analytical techniques that were used is as follows:

Ion Chromatography System (ICS)

The Ion Chromatography System (ICS) was used to determine the concentration of ions in both RSS and leaching test eluate samples. The Ion Chromatography System (ICS) undertakes isocratic ion analyses using suppressed conductivity detection. The ion chromatography system typically consists of six main elements including a liquid eluent, a high-pressure pump, a sample injector, a separator column, a chemical suppressor, and a conductivity cell. Prior to testing a sample, a standard solution is used to calibrate the ICS. The data obtained from a sample is compared to that obtained from the standard calibration solution, and ions can be identified and quantitated. Each peak in a chromatogram is automatically converted to a sample concentration, using specialised computer software, and a tabulated printout of the results is produced (Figure 3.24) (Dionex Corporation, 2004). In this experimental programme, Dionex ICS-90 was used (Figure 3.25).

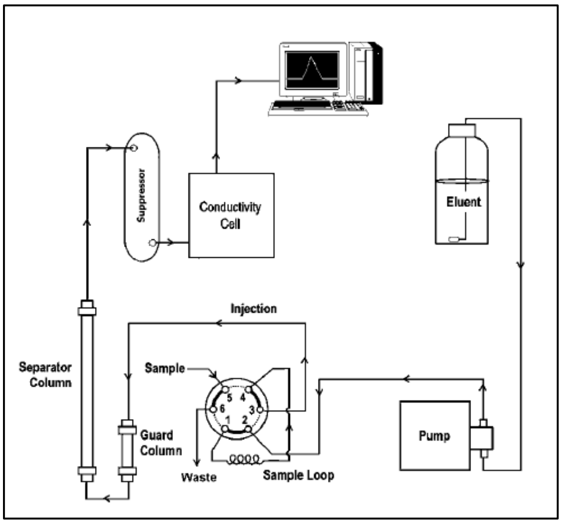


Figure 3.24: Ion analysis process (Dionex Corporation, 2004).

Figure 3.25: Dionex ICS-90.

Inductively coupled plasma (ICP)

The inductively coupled plasma spectrometer was used to determine the concentration of heavy metals in both RSS and leaching test eluate samples. The inductively coupled plasma spectrometer is a tool used to detect trace elements in solution, in which liquid samples are injected into argon gas plasma contained by a strong magnetic field. The argon gas plasma excites elements in the sample and energy is emitted from the electrons at a characteristic wavelength as they return to ground state. The optical spectrometry measures the emitted light (Figure 3.26). This method, known as inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled optical emission spectrometry (ICP-OES), is a very effective technique used for identification and quantification of elements in a sample (Labcompare, 2013). In this experimental programme, SPECTRO CIROS^{CCD} Nr. ICP-32 was used (Figure 3.27).

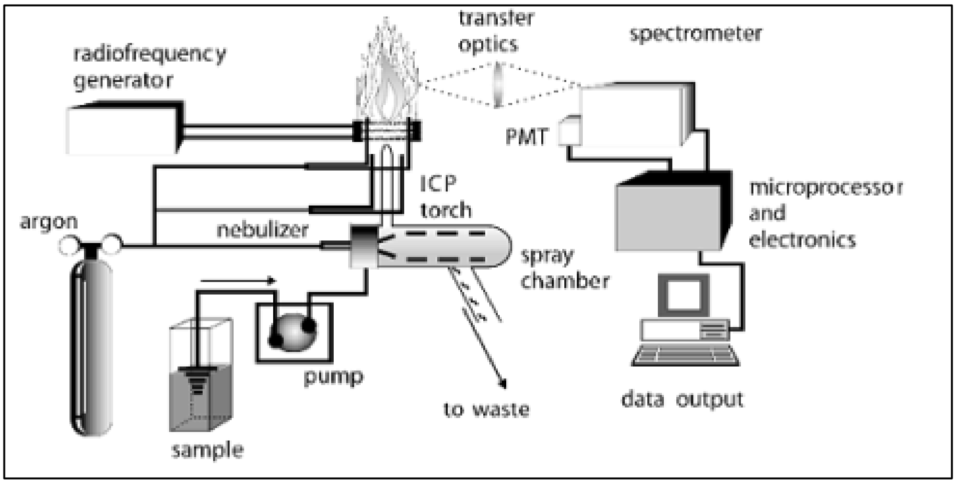


Figure 3.26: Inductively coupled plasma-atomic emission spectrometer ICP-AES (The Baltic University, 2013).

Figure 3.27: SPECTRO CIROS^{CCD} Nr. ICP-32.

<u>**X-Ray Fluorescence (XRF)**</u>

The X-Ray Fluorescence (XRF) spectrometer was used to analyse the chemical composition of dry samples, such as dry sewage sludge and unprocessed fly ash. The X-Ray Fluorescence (XRF) spectrometer is an x-ray instrument used to detect elements in solid, liquid and powdered samples. It is a non-destructive method that can be used for a wide range of elements, from sodium to uranium, and provides detection limits at the sub-ppm level; as well as it can measure higher concentrations of up to 100% (Spectro, 2013). The XRF method mainly depends on interactions between electron beams and x-rays with samples. Materials can become ionized when they are excited with high-energy and short wavelength radiation (e.g., X-rays). The radiation energy frees a tightly-held inner electron, consequently the atom becomes unstable and an outer electron replaces the missing inner electron. As a result of this, energy is released due to difference in binding energy of the inner electron orbital and the outer one. The produced radiation is of lower energy than the main incident X-rays and is called fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the elements that are existing in the sample (Figure 3.28) (Geochemical Instrumentation and Analysis, 2013). In this experimental work, SPECTRO XEPOS XRF system was used (Figure 3.29).

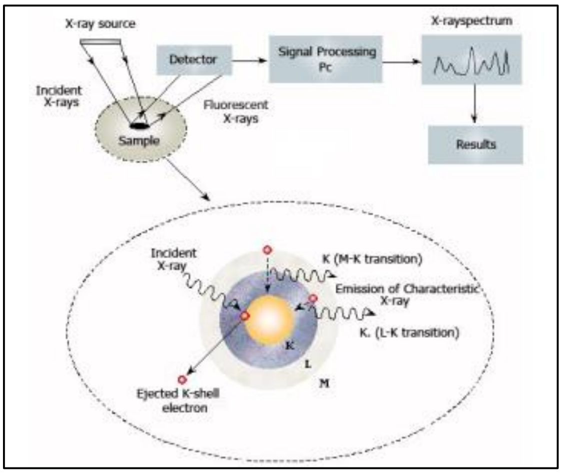


Figure 3.28: The principle of XRF and the typical XRF detection arrangements (Ocean King India, 2013).

Figure 3.29: SPECTRO XEPOS XRF system.

Thermo-Gravimetric Analysis (TGA)

TGA was used to obtain the Loss On Ignition (LOI) for both unprocessed fly ash and dry sewage sludge samples between 100 and 800^{o}C. TGA is a destructive test that uses heat to force materials to react and therefore causes physical changes to occur. TGA measures mass change in materials that happen due to transition and thermal degradation. TGA records changes in mass due to dehydration, decomposition, and oxidation of a sample with time and temperature.

Scanning Electron Microscopes (SEM)

SEM was used to obtain magnified images of the unprocessed fly ash samples. A SEM is a type of electron microscope that uses focused beam of electrons to produce magnified images of a sample. A reaction happens between the focused beam of electrons and electrons in the sample, producing various signals that can be detected and used to obtain images for the sample's surface. This technique is also used to obtain chemical composition for samples (Figure 3.30) (Purdue University, 2013). In this experimental programme, ZEIZZ Evo 50 was used (Figure 3.31).

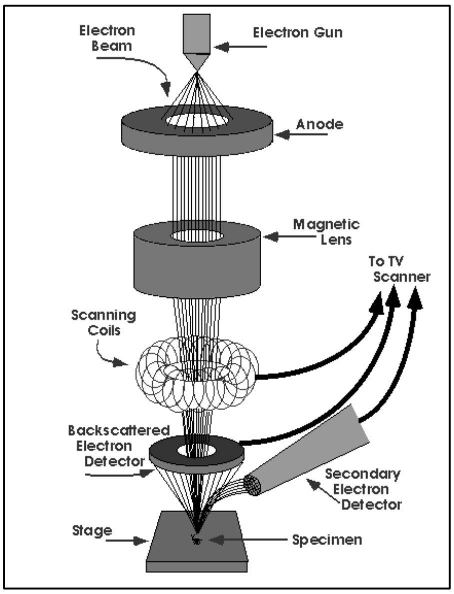


Figure 3.30: The principles of SEM (Purdue University, 2013).

Figure 3.31: ZEISS Evo 50 SEM.

CHAPTER 4: FRESH AND PHYSICAL PROPERTIES

4.1 INTRODUCTION

Long-term properties of hardened concrete, such as strength, volume stability and durability, are significantly affected by the properties and mixing proportions of used materials. Long-term properties are also affected by the degree of compaction, which is directly associated with the workability of fresh mixes. Workability can be defined as the amount of useful internal work necessary to produce a good quality concrete that can be properly compacted and also can be transported, placed and finished sufficiently without any segregation. Workability of cement-based mixes depends on a number of related factors including water content, aggregate type and grading, aggregate/cement ratio, fineness of cement and also depends on other factors including the presence of admixtures. The compaction degree along with water content and the grading of fine particles in concrete mixes contribute to the volume of voids in hardened concrete, as void in hardened concrete are either bubbles of entrapped air or spaces left after excess water has been evaporated. Thus the presence of voids in concrete reduces the density and consequently reduces compressive strength: 5% of voids can reduce the compressive strength by as much as 30% (Neville and Brooks, 2004).

The examination of the physical properties including workability, Total Water Absorption (TWA) and density is the first stage to identify the potential utilisation of RSS and unprocessed fly ash in cement-based materials. Workability is an important parameter when considering compaction and consistency of produced mixes. TWA is an indirect way to measure voids and porosity in mortar and concrete mixes, which influences density and other mechanical and durability properties.

4.2 AIMS AND OBJECTIVES

This chapter focuses on the evaluation of the physical properties of cement-based materials that incorporated Raw Sewage Sludge (RSS) and unprocessed fly ash. Physical properties include flowability/workability, total water absorption and density, which were examined for three series of cement-based materials throughout this experimental programme. Cement-based materials included mortar mixes with unprocessed fly ash (Series 1), mortar mixes with large proportion of unprocessed fly ash (Series 2) and concrete mixes with RSS and unprocessed fly ash (Series 3). RSS was used as a water replacement in all the series stated above.

4.3 MATERIALS, MIXING PROPORTIONS, PREPARATIONS AND TESTING

The materials that were used throughout the experimental work included Portland cement, fine aggregate (sand), coarse aggregate (gravel), drinking water, Raw Sewage Sludge (RSS) and unprocessed fly ash. More details about used materials are available in Section 3.3.

Three series of cement-based mixes were tested for their fresh and physical properties including mortar mixes with RSS and unprocessed fly ash (Series 1), mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2), and concrete mixes with RSS and unprocessed fly ash (Series 3). All groups in Series 1 were investigated. The mixing proportions of the investigated series are described in more details in Section 3.3.10.

Steel moulds (50mm in size) were used to cast mortar samples for TWA and density. Mortar samples were prepared and compacted manually in accordance to ASTM C109/C109M-08 (ASTM, 2008). For concrete mixes, 100mm in size steel moulds were used for the determination of TWA (the mould was divided into two halves of 100x100x50 mm each using a steel divider) and density. Cast specimens were covered with plastic sheets and placed in a room at a temperature of 20$\pm$2 ^oC for 24 hours until demoulding. Thereafter, samples were wrapped by either a cling film (for mortar sampler) or plastic sheets (for concrete samples) until testing. More details about mixes preparation, mixing and casting are available in section 3.4.

Flow table that complies with BS EN 1015-3:1999 (BSI, 1999a) was used to obtain flowability for mortar mixes. The workability for concrete samples was obtained using slump test in accordance to BS EN 12350-2:2009 (BSI, 2009a). The density of mortar specimen was obtained by recording the mass of cured samples to the nearest 0.01g. Volume of samples was obtained manually using an accurate calibre that was used to measure length, width and height. Density was calculated using Equation 3.1, and the average of three specimens was recorded to the nearest 1 Kg/m^3. For concrete specimens, density was obtained in accordance to BS EN 12390-7:2009 (BSI, 2009d). Mass of concrete samples was recorded in Kg to the nearest 0.01 % of the mass of the specimen and volume was obtained by water displacement method using stirrup arrangement. Density was calculated using Equations 3.1 and 3.2, and the average of two specimens was recorded to the nearest 1 Kg/m^3. For the determination of TWA, 50x50x50 mm in size specimens were used for mortar mixes, whereas 50x100x100mm in size specimens were used for concrete samples. Cured specimens were dried in an electrical oven at 75^oC until a constant weight. Thereafter, dried specimens were placed at a room temperature for two hours to cool down, and mass was later measured and recorded to the nearest 0.1g. Dried samples were immersed in water until a constant weight (weight was monitor at different times). Prior to measuring mass of saturated samples, external surfaces were manually dried using damp towels. Total water absorption was calculated using Equation 3.3, and was recorded to the nearest 0.01% (the average of three mortar specimen and two concrete specimens). More details are available in Sections 3.5.1, 3.5.2 and 3.5.3.

4.4 RESULTS

4.4.1 Flowability/Workability

4.4.1.1 Series 1: Mortar mixes with RSS and unprocessed fly ash

The flowability results of this series are presented in Table 4.1. The flowability results of each group of mixes are as follows:

Influence of RSS (Group 1)

The flowability of the mortar mixes with different RSS content is shown in Figure 4.1. In this group, four mortar mixes (M1, M2, M3 and M4) that incorporated a constant sand to cement ratio of 4.5, 0% unprocessed fly ash and four RSS/Cement ratios of 0.5, 0.65, 0.8 and 1 were investigated. For comparison purposes, M14 (which contained drinking water equivalent to the water content of M3), was also evaluated. The figure clearly shows that the flowability of mortar mixes increased when the content of RSS increased, and the greatest flow value of 233mm was recorded for the mortar mix with RSS/Cement ratio of 1 (M4). The results also showed that the workability of the mortar mix that incorporated RSS (M3) was 9% less than that made with drinking water (M14) (Figure 4.6 and Table 4.2).

Table 4.1: Flowability of mortar mixes with RSS and unprocessed fly ash (Series 1).

Mix	Flowability (mm)
M1	120
M2	130
M3	178
M4	233
M5	230
M6	130
M7	125
M8	133
M9	123
M10	113
M11	123
M12	115
M13	107
M14	195
M15	150
M16	125
M17	115

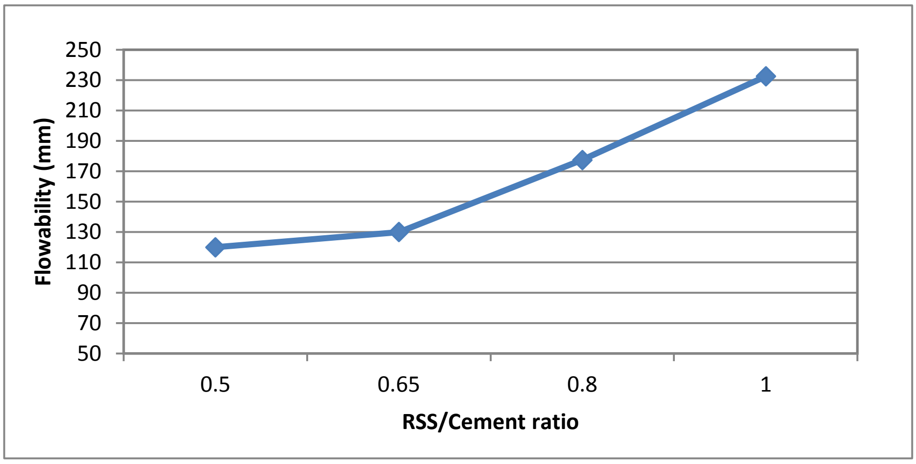


Figure 4.1: Flowability of mortar mixes with different RSS/Cement ratios (Group 1).

Influence of sand content (Group 2)

The influence of varying sand content on flowability for mortar mixes is shown in Figure 4.2. In this group, four mixes, that contained a constant RSS/Cement ratio of 0.8 and four sand to cement ratios of 3, 4.5, 6 and 7.5 (M5, M3, M6 and M7 respectively), were investigated. The results showed that the flowability of mortar mixes decreased when the sand content increased and the greatest flowability value of 230mm was recorded for the mortar mix with the sand to cement ratio of 3 (M5).

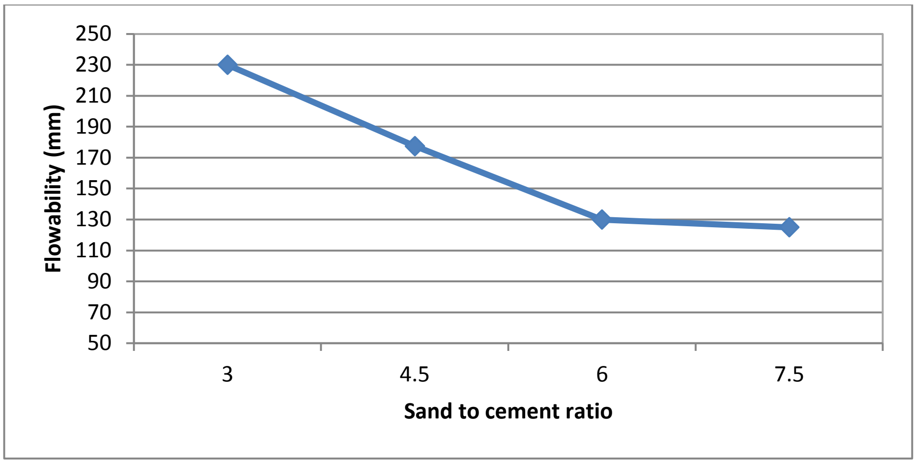


Figure 4.2: Flowability of mortar mixes with different sand to cement ratios.

Influence of fly ash (Group 3 and 4)

Flowability for mortar mixes that incorporated RSS and different proportions of unprocessed fly ash is shown in Figure 4.3 and Figure 4.4. Two groups of mortar mixes that contained a constant sand to binder ratio of 4.5 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder), were examined. The RSS/Binder ratio for Group 3 (M2, M11, M12 and M13) was 0.65 whereas for Group 4 (M3, M8, M9 and M10) was 0.8. Both figures clearly demonstrate that the flowability of mortar mixes reduced when the content of unprocessed fly ash increased for both RSS/Binder ratios. The lowest flowability value for Group 3 was recorder for the mix with 30% unprocessed fly ash replacement (M13), which was 107mm. The lowest reading for Group 4 was also recorded for the mix with 30% unprocessed fly ash replacement (M10), which was 113mm. In addition, the results exhibited that the reduction of RSS content significantly influenced flowability of mortar mixes without unprocessed fly ash, but less impact was observed for mixes the contained unprocessed fly ash.

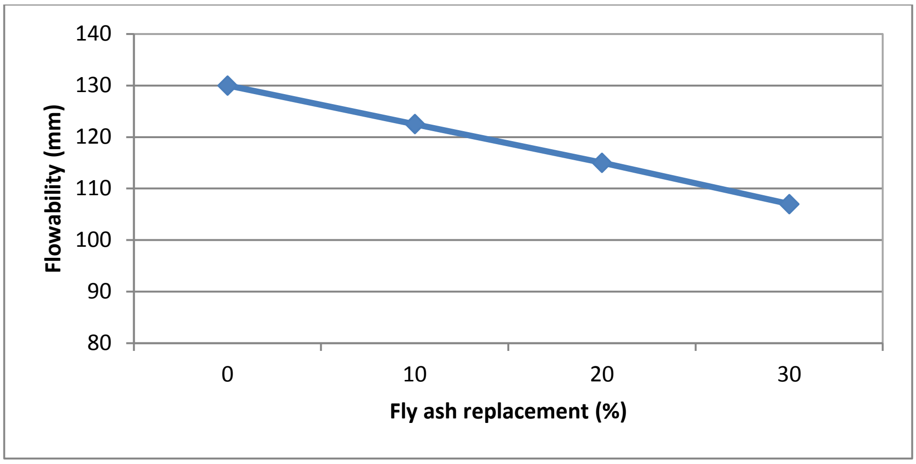


Figure 4.3: Flowability of mortar mixes with different unprocessed fly ash replacement and RSS/Binder ratio of 0.65 (Group 3).

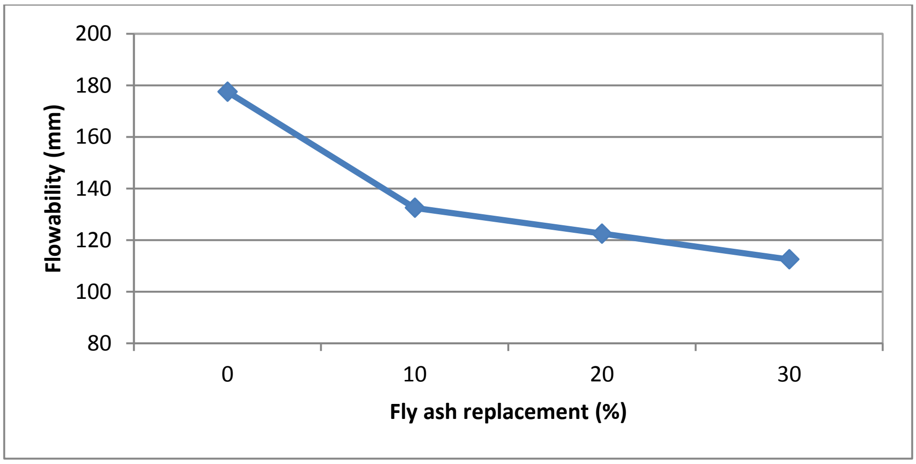


Figure 4.4: Flowability of mortar mixes with different unprocessed fly ash replacement and RSS/Binder ratio of 0.8 (Group 4).

Influence of fly ash in the control (Group 5)

Flowability of the control mixes is shown in Figure 4.5. This group of mixes (M14, M15, M16 and M17) contained a constant sand to binder ratio of 4.5, Water/Binder ratio of 0.8 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder). The figure clearly shows that the flowability of mortar mixes decreased when the content of unprocessed fly ash increased, and the greatest flowability value of 195mm was recorded for the mortar mix with 0% unprocessed fly ash (M14).

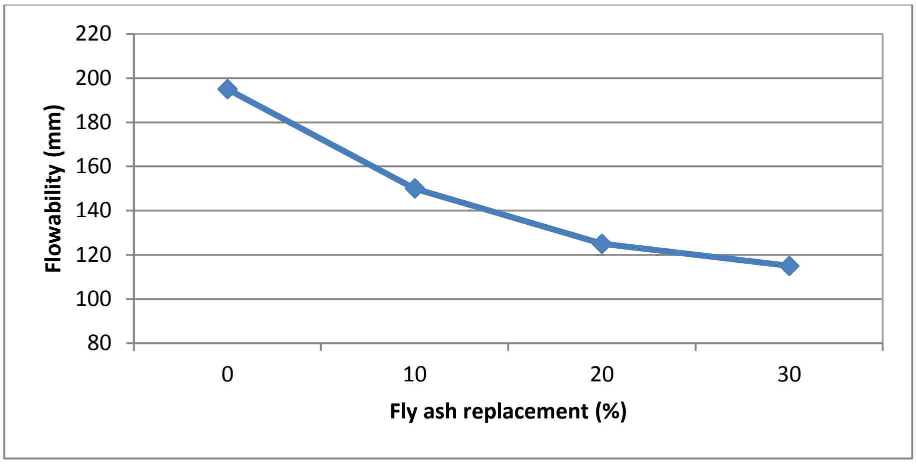


Figure 4.5: Flowability of control mixes with different unprocessed fly ash replacements and Water/Binder ratio of 0.8 (Group 5).

Flowability of mortar mixes that contained both water and RSS is shown in Figure 4.6, and the relative flowability of mortar mixes made with RSS in comparison to those made with water is shown in Table 4.2. Both show minor differences in flowability for mixes with 0 and 10% unprocessed fly ash and no significant differences at higher unprocessed fly ash replacement.

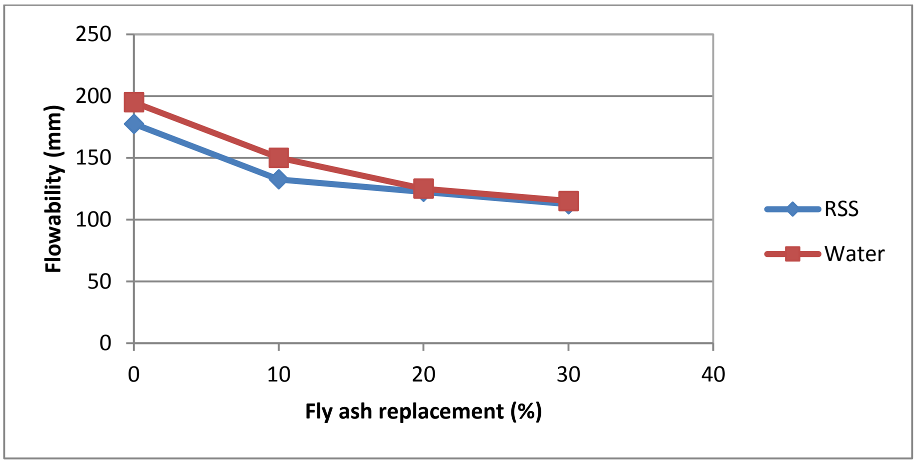


Figure 4.6: Flowability of mortar mixes with water and RSS.

Table 4.2: Relative flowability (%) of mortar mixes with RSS in comparison to those made with water.

Mixes	Fly ash %	Relative flowability (%)
M3/M14	0	91
M8/M15	10	88
M9/M16	20	98
M10/M17	30	98

4.4.1.2 Series 2: Mortar mixes with large proportions of unprocessed fly ash

Flowability results of this series are presented in Table 4.3 and Figure 4.7. Four mixes, that contained a constant sand to binder ratio of 4.5 and a constant Water/Binder ratio of 1, were examined. One more control mix that contained drinking water and 0% unprocessed fly ash replacement was also investigated for comparison purposes. Cement was replaced with 0, 40, 60 and 80% unprocessed fly ash by weight of total binder. The figure clearly shows that the flowability was significantly reduced when unprocessed fly ash content increased. Figure 4.8 shows that flowability of the mortar mix that made with RSS (ML1) water was comparatively less than that made with water (MLRef). The flowability of ML1 is 20.8% less than that for MLRef).

Table 4.3: Flowability of mortar mixes with large proportion of unprocessed fly ash (Series 2).

Mix	Flowability (mm)
MLRef	300
ML1	237.5
ML2	130
ML3	100
ML4	100

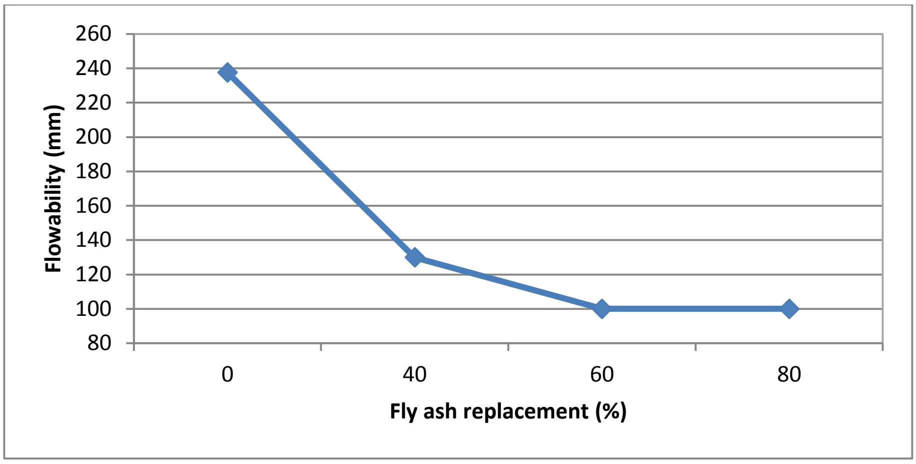


Figure 4.7: Flowability of mortar mixes with RSS and large proportion of unprocessed fly ash (Series 2).

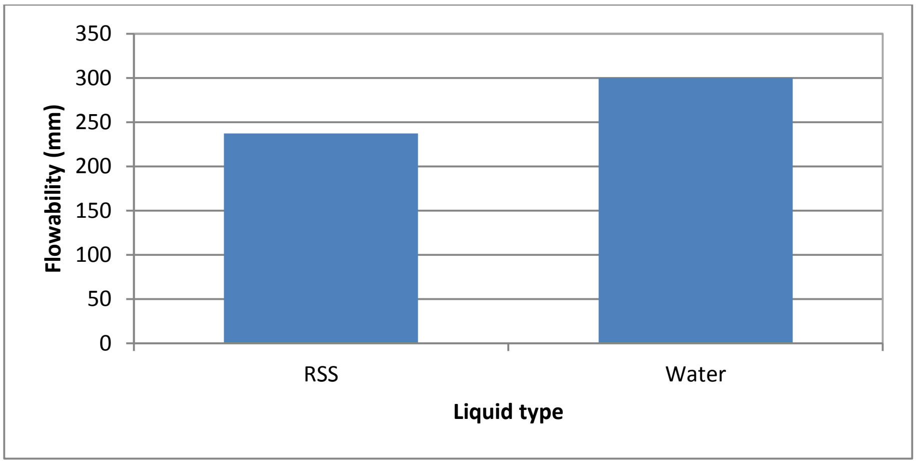


Figure 4.8: Flowability of mortar mixes with RSS and water (Series 2).

4.4.1.3 Series 3: Concrete mixes with RSS and unprocessed fly ash

The workability of the concrete mixes is shown in Table 4.4 and Figure 4.9. This Series included four concrete mixes that incorporated a constant cement:sand:gravel ratio of 1:1.5:3 respectively and a constant liquid to binder ratio of 0.5. Cement was replaced with 0, 10, 15, 20% unprocessed fly ash by weight of total binder. One control mix made of drinking water with 0% unprocessed fly ash was also evaluated. The figure clearly shows that the workability of concrete mixes significantly reduced when unprocessed fly ash content was included. The results also showed that workability of the concrete mix that was made with RSS was 31.4% less than that made with water, and this is presented in Figure 4.10. The greatest slump value of 120mm was recorded for the mix with 0% unprocessed fly ash (CM1) and the lowest slump value of 5mm was recorder for the mix with 20% unprocessed fly ash replacement (CM4).

Table 4.4: Workability of concrete mixes (Series 3).

Mix	Fly ash %	Slump (mm)
CMRef	0	175
CM1	0	120
CM2	10	55
CM3	15	12
CM4	20	5

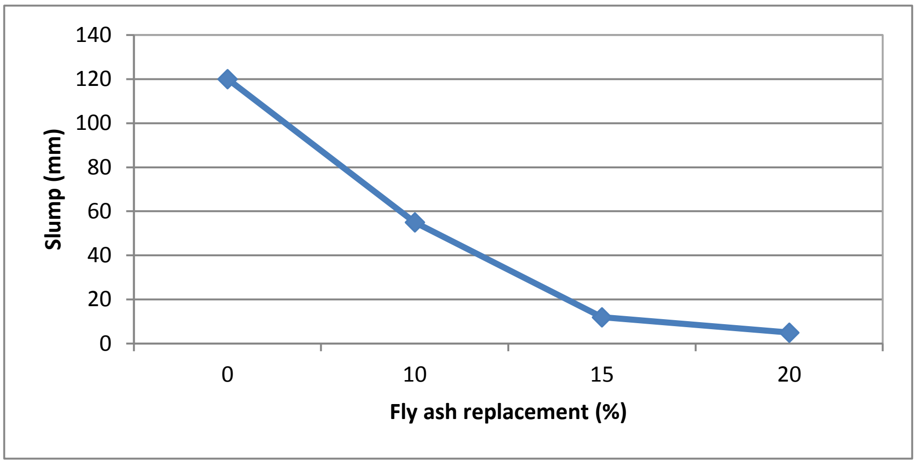


Figure 4.9: Workability of concrete mixes with RSS and unprocessed fly ash (Series 3).

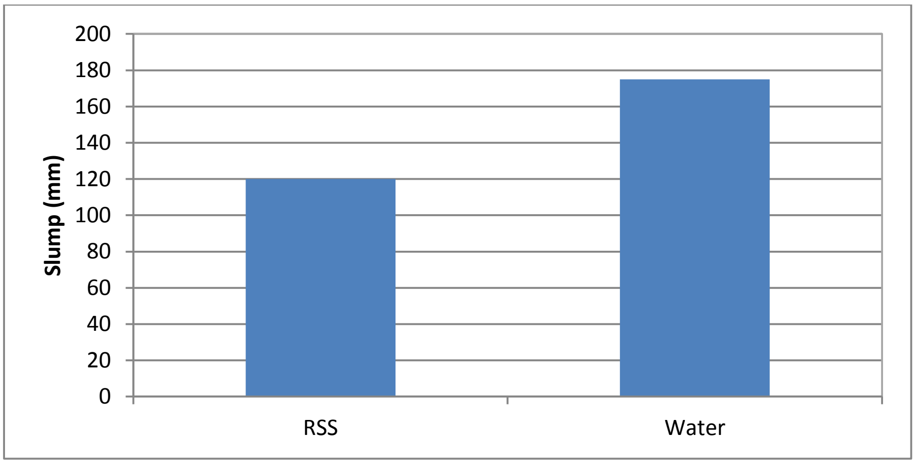


Figure 4.10: Workability of concrete mixes with RSS and water (Series 3).

4.4.2 Density

4.4.2.1 Series 1: Mortar mixes with RSS and unprocessed fly ash

The density results of this series are presented in Table 4.5. The density results of each group of mixes are as follows:

Influence of RSS (Group 1)

The density of the mortar mixes with different RSS content is presented in Figure 4.11. This group of mixes (M1, M2, M3 and M4) incorporated a constant sand to cement ratio of 4.5, 0% unprocessed fly ash and four RSS/Cement ratios of 0.5, 0.65, 0.8 and 1. For comparison purposes, M14 (which contained drinking water equivalent to the water content of M3), was also evaluated. Density was recorded for mortar specimens at 1, 7, 28, 90 and 365 days, and the average density was also determined. The results showed that the density decreased when the content of RSS increased. The results also showed that density varied with curing age for the same mix. The average density of mortar mixes decreased when the content of RSS increased, and the greatest average density of 2249kg/m^3 was recorded for the mortar mix with RSS/Cement ration of 0.5 (M1). The results also showed that density of the mortar mix that contained drinking water (M14) was comparatively higher than that made of RSS (M3), as the average density of M14 was 2130kg/m^3 and for M3 was 2072kg/m^3 (Figure 4.16A).

Table 4.5: Density of mortar mixes with RSS and unprocessed fly ash in Kg/m^3 (Series 1).

Mix	Density (Kg/m^3)					
	1 day	7 days	28 days	90 days	365 days	Average
M1	2241	2283	2281	2243	2199	2249
M2	2256	2263	2195	2164	2137	2203
M3	2104	2123	2090	2051	1989	2072
M4	2047	1989	1990	1930	1885	1968
M5	2063	2047	1983	1936	1886	1983
M6	2209	2235	2198	2118	2083	2169
M7	2203	2175	2171	2131	2056	2147
M8	2156	2123	2079	2047	2021	2085
M9	2168	2133	2116	2073	2013	2101
M10	2120	2120	2108	2023	1982	2071
M11	2227	2236	2199	2144	2134	2188
M12	2212	2193	2194	2154	2111	2173
M13	2170	2163	2138	2077	2053	2120
M14	2168	2185	2163	2076	2057	2130
M15	2162	2193	2177	2154	2118	2161
M16	2146	2143	2131	2176	2098	2139
M17	2156	2155	2143	2154	2125	2147

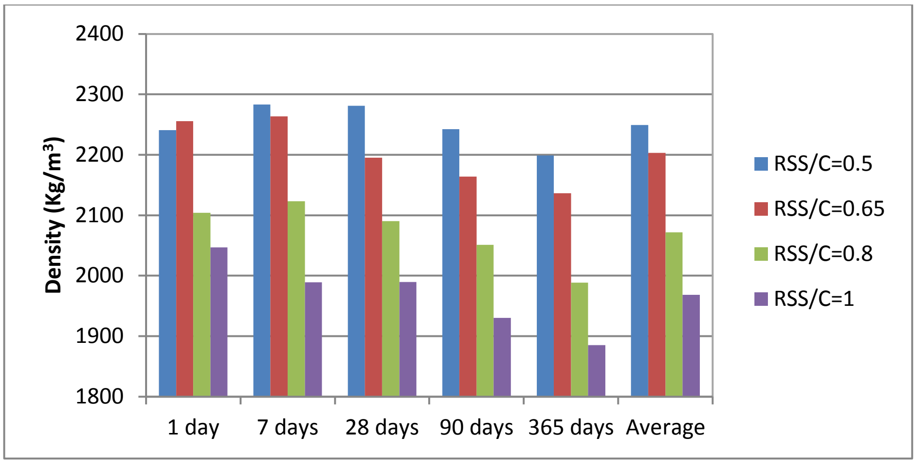


Figure 4.11: Density of mortar mixes with different RSS content (Group 1).

Influence of sand content (Group 2)

The influence of varying sand content on the density of hardened mortar is shown in Figure 4.12. Four mixes, that contained a constant RSS/Cement ratio of 0.8 and four sand to cement ratios of 3, 4.5, 6 and 7.5 (M5, M3, M6 and M7 respectively), were investigated. The results presented that the density increased when the sand to cement ratio increased up to 6 at all curing ages except at 90 days. Some variations in density with curing age for the same mix were observed. The average density steadily increased when the sand content increased (up to sand to cement ratio of 6) and the best average density of 2169 Kg/m^3 was recorded for M6.

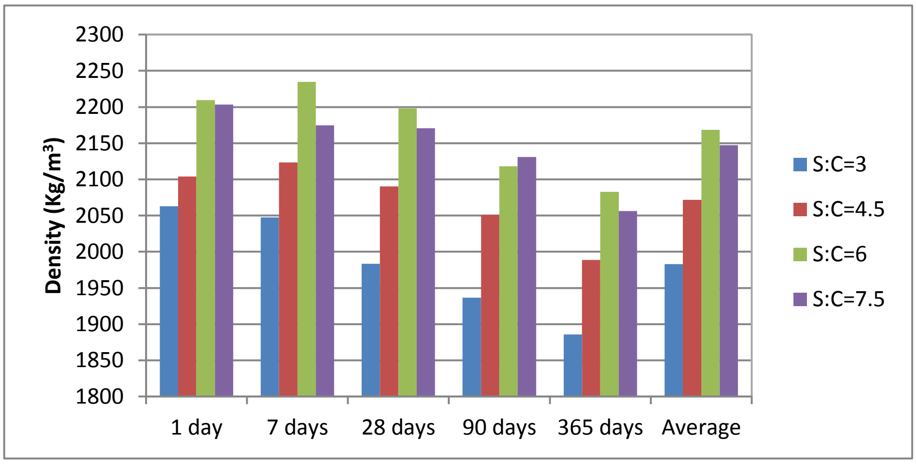


Figure 4.12: Density of mortar mixes with different sand content (Group 2).

Influence of fly ash (Groups 3 and 4)

The density results for Group 3 and 4 are presented in Figure 4.13 and Figure 4.14. Two groups of mortar mixes that contained a constant sand to binder ratio of 4.5 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder), were examined. Group 3 (M2, M11, M12 and M13) was prepared with RSS/Binder ratio of 0.65 whilst Group 4 (M3, M8, M9 and M10) was prepared with RSS/Binder ratio of 0.8. For Group 3, the results demonstrated that the density generally decreased when the content of unprocessed fly ash increased. The greatest density was recorded for the mortar mix with 0% unprocessed fly ash at all ages (except 28 days). The average density steadily decreased when the unprocessed fly ash content increased and the greatest average density of 2203 kg/m^3 was recorded for the mortar mix with 0% unprocessed fly ash (M2). For Group 4, the results presented that the density increased when the content of fly ash increased and the greatest density was observed for the mortar mix with 20% unprocessed fly ash (M9). The average density steadily increased when the fly ash content increased (up to 20% cement replacement), and the greatest average density of 2101 Kg/m^3 was recorded for the mortar mix with 20% unprocessed fly ash (M9). The results also showed a noticeable variation in density with curing age for the same mix. Additionally, the results showed that the density generally decreased when the content of RSS/Binder ratio increased.

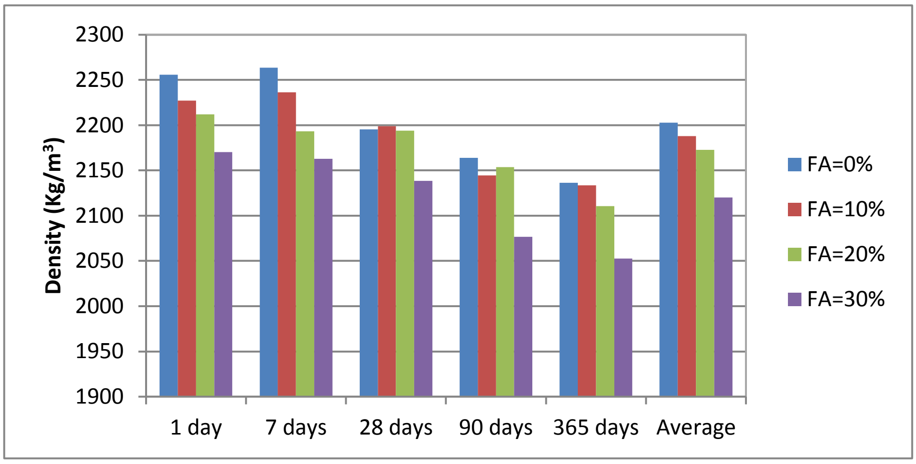


Figure 4.13: Density of mortar mixes with different unprocessed fly ash replacement and RSS/Binder ratio of 0.65 (Group 3).

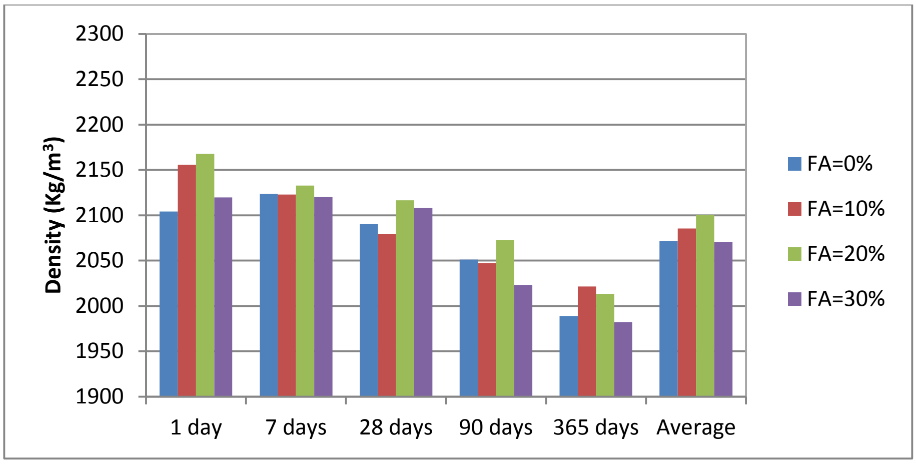


Figure 4.14: Density of mortar mixes with different unprocessed fly ash replacement and RSS/Binder ratio of 0.8 (Group 4).

Influence of fly ash in the control (Group 5)

The density of the control mixes is shown in Figure 4.15. This Group (M14, M15, M16 and M17) included four mixes that contained the same composition of Group 4 but with water. The results showed a noticeable variation in density with curing age for the same mix; however, the average results showed that the addition of unprocessed fly ash improved density and the greatest density was achieved when 10% unprocessed fly ash was used. The greatest average density of 2161 kg/m^3 was recorded for mortar mix with 10% unprocessed fly ash (M15).

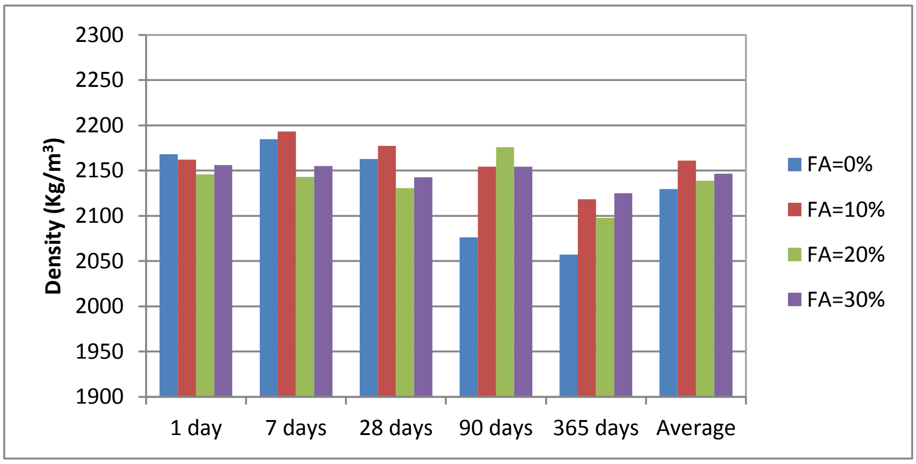
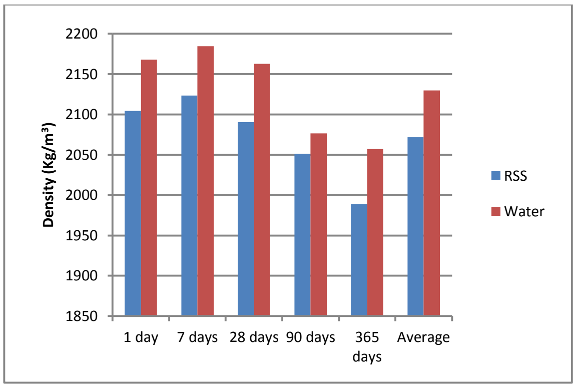
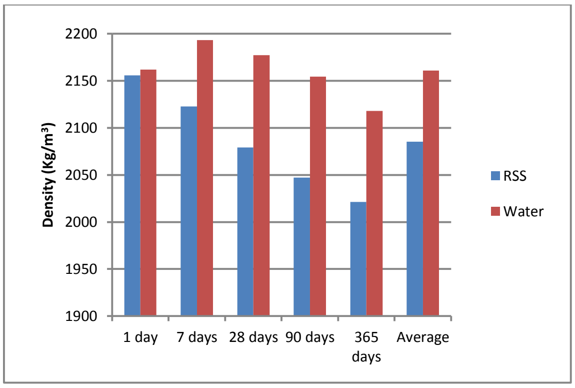


Figure 4.15: Density of control mixes with different unprocessed fly ash replacements and Water/Binder ratio of 0.8 (Group 5).

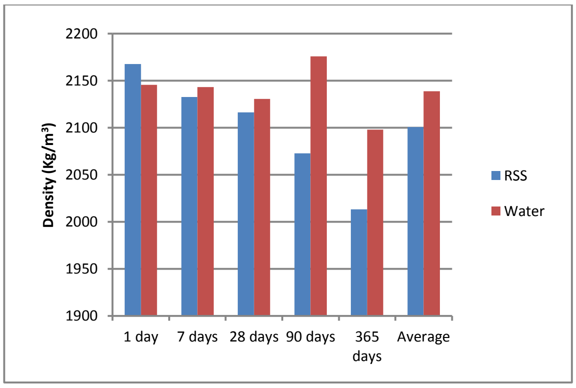
The density of the mortar mixes with RSS and water (Group 4 and Group 5) is shown in Figure 4.16, and the relative density is presented in Table 4.6. Both show no significant differences in density between mixes contained RSS and those made with water as the relative density ranged between 93.3-101%.



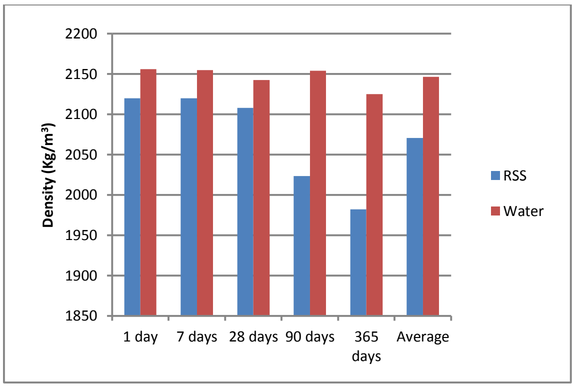
A: 0% unprocessed fly ash



B: 10% unprocessed fly ash



C: 20% unprocessed fly ash



D: 30% unprocessed fly ash

Figure 4.16: Density of mortar mixes that with RSS and water.

Table 4.6: Relative density (%) of mortar mixes with RSS in comparison to those made with water (Series 1).

Mixes	Fly ash %	Relative density (%)					
		1 day	7 days	28 days	90 days	365 days	Average
M3/M14	0	97.1	97.2	96.7	98.8	96.7	97.3
M8/M15	10	99.7	96.8	95.5	95.0	95.4	96.5
M9/M16	20	101.0	99.5	99.3	95.3	96.0	98.2
M10/M17	30	98.3	98.4	98.4	93.9	93.3	96.5

4.4.2.2 Series 2: Mortar mixes with large proportions of unprocessed fly ash

Table 4.7 and Figure 4.17 show the density of mortar mixes with large proportions of unprocessed fly ash. Four mixes, that contained a constant sand to binder ratio of 4.5 and Water/Binder ratio of 1, were examined. One more mix that contained drinking water was also evaluated and considered as the control. Cement was replaced with 0, 40, 60 and 80% unprocessed fly ash by weight of total binder. Samples were tested at 1, 7, 28, 90 and 180 days. The results showed that density varied with curing age for the same mix. The results also showed that the greatest density (and average density) was achieved when cement was replaced with 40% unprocessed fly ash (ML2) at all curing age. The density of the control mix was comparatively higher than that for the mix with RSS (Figure 4.18). No significant differences in density between mixes contained RSS and those made with water were observed as the relative density ranged between 94.4-98.2% (Table 4.8).

Table 4.7: Density of mortar mixes with RSS and large proportions of unprocessed fly ash in Kg/m³ (Series 2).

Mix	Fly ash %	Density (Kg/m³)					
		1 day	7 days	28 days	90 days	180 days	Average
MLRef	0	2148	2113	2103	2093	2037	2099
ML1	0	2028	2040	2042	2009	2001	2024
ML2	40	2062	2099	2075	2058	2008	2061
ML3	60	ND	2052	2058	2019	1992	2030
ML4	80	ND	2027	1996	1978	1923	1981

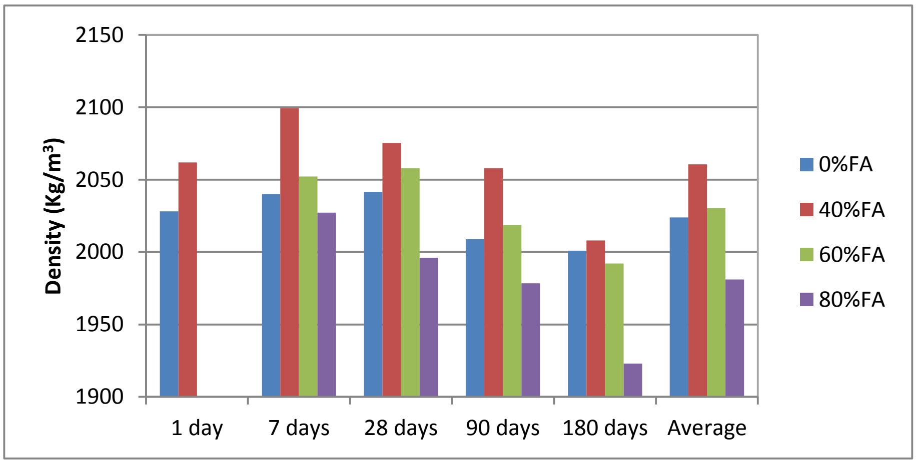


Figure 4.17: Density of mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2).

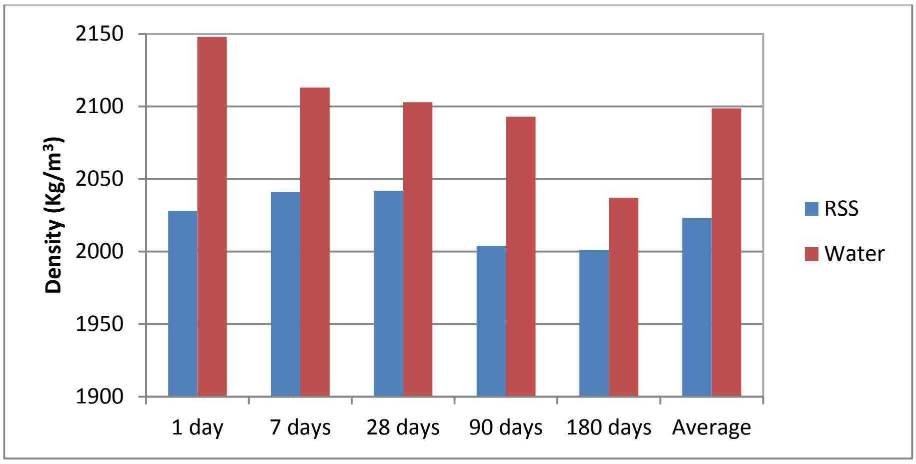


Figure 4.18: Density of mortar mixes with RSS and water (Series 2).

Table 4.8: Relative density (%) of mortar mixes with RSS in comparison to those made with water (Series 2).

Mixes	Fly ash %	Relative density (%)					
		1 day	7 days	28 days	90 days	180 days	Average
ML1/MLRef	0	94.4	96.5	97.1	96	98.2	96.4

4.4.2.3 Series 3: Concrete mixes with RSS and unprocessed fly ash

The density of the concrete mixes is shown in Table 4.9 and Figure 4.19. This Series included four mixes that incorporated a constant cement:sand:gravel ratio of 1:1.5:3 respectively and Liquid/Binder ratio of 0.5. Cement was replaced with 0, 10, 15 and 20% unprocessed fly ash by weight of total binder. One more mix (CMRef) that was made with drinking water was evaluated and considered as the control. Specimens were cured and tested for their density at 1, 7, 28, 90 and 300 days. The result showed a noticeable variation in density with curing age for all mixes, however a clear trend was observed for the average density. The average results showed that density of concrete mixes increased when the content of unprocessed fly ash increased up to 15%, and the greatest average density of 2302 Kg/m^3 was recorded for the concrete mix with 15% unprocessed fly ash (CM3). The density of the control mix (CMRef) was comparatively greater than that made with RSS (CM1) (Figure 4.20). The relative density ranged between 94.1-95% (Table 4.10).

Table 4.9 : Density of concrete mixes with RSS and unprocessed fly ash in Kg/m^3 (Series 3).

Mix	Fly ash %	Density (Kg/m^3)					
		1 day	7 days	28 days	90 days	300 days	Average
CMRef	0	2359	2372	2363	2378	2347	2364
CM1	0	2236	2233	2245	2250	2229	2238
CM2	10	2308	2272	2284	2251	2269	2277
CM3	15	2328	2315	2287	2298	2284	2302
CM4	20	2308	2272	2284	2251	2292	2281

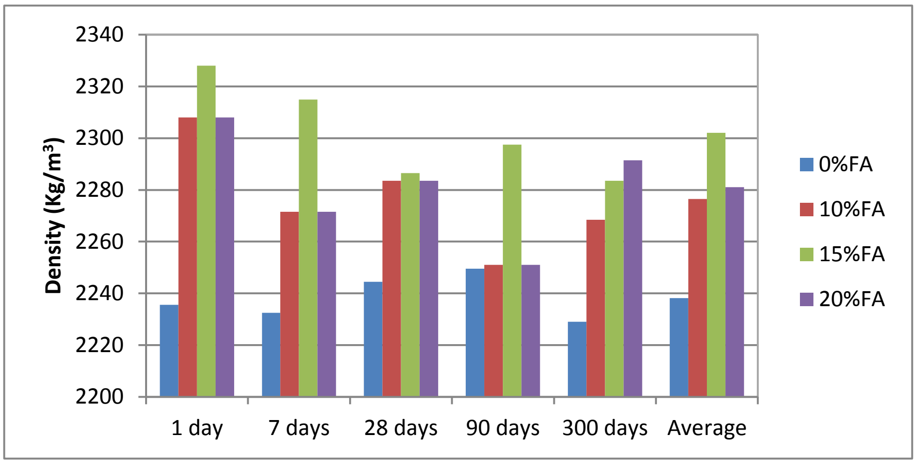


Figure 4.19: Density of concrete mixes with RSS and unprocessed fly ash (Series 3).

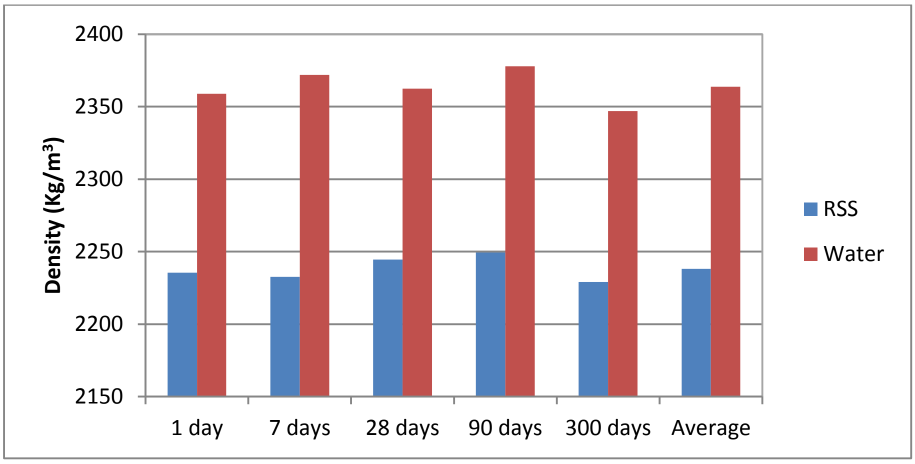


Figure 4.20: Density of concrete mixes with RSS and water (Series 3).

Table 4.10: Relative density (%) of concrete mixes with RSS in comparison to those made with water (Series 3).

Mixes	Fly ash %	Relative density (%)					
		1 day	7 days	28 days	90 days	300 days	Average
CM1/CMRef	0	94.8	94.1	95	94.6	95	94.7

4.4.3 Total Water Absorption (TWA)

4.4.3.1 Series 3: Mortar mixes with RSS and unprocessed fly ash

The TWA results of this series are presented in Table 4.11. The TWA results of each group in this series are as follows:

Influence of RSS (Group 1)

Figure 4.21 shows the TWA values of mortar mixes with different RSS content. This group consisted of four mixes (M1, M2, M3 and M4) that incorporated a constant sand to cement ratio of 4.5, 0% unprocessed fly ash and four RSS/Cement ratios of 0.5, 0.65, 0.8 and 1. For comparison purposes, M14 (which contained drinking water equivalent to the water content of M3), was evaluated and considered as the control. TWA was recorded for mortar specimens at 1, 7, 28, 90 and 365 days, and the average TWA was determined. The results showed that TWA generally decreased with age until 365 days for all mixes in this group except for M14. However a clear trend in TWA was observed, as TWA increased when the RSS content increased and the greatest average TWA of 11.6% was recorded for the mortar mix with RSS/Cement ratio of 1 (M4). The results also showed that TWA for the control mix (M14) was relatively higher than that made with RSS (M3), as TWA for M14 was 10.1% and for M3 was 9.7 (Figure 4.26A).

Table 4.11: TWA of mortar mixes with RSS and unprocessed fly ash (Series 1).

Mix	TWA (% dry weight)					
	1 day	7 days	28 days	90 days	365 days	Average
M1	7.6	6.9	6.4	6.4	7.0	6.9
M2	8.4	7.8	7.6	7.4	7.8	7.8
M3	10.3	9.8	9.6	9.4	9.6	9.7
M4	12.2	11.9	11.0	11.2	11.9	11.6
M5	13.0	12.1	11.8	11.0	12.0	12.0
M6	8.6	8.1	7.8	7.5	8.2	8.0
M7	7.8	7.4	7.0	6.8	8.3	7.4
M8	10.7	9.6	8.5	9.1	8.3	9.2
M9	10.7	9.6	9.5	9.2	11.2	10.0
M10	10.8	10.2	10.1	9.9	10.6	10.3
M11	8.8	8.6	8.2	7.8	8.5	8.4
M12	9.0	8.5	8.2	7.9	8.8	8.5
M13	9.7	9.1	8.8	8.2	9.7	9.1
M14	11.0	10.2	9.9	9.7	9.6	10.1
M15	11.0	10.4	10.0	9.5	10.4	10.3
M16	11.4	10.5	10.0	9.9	11.0	10.6
M17	11.0	10.8	10.9	10.5	11.8	11.0

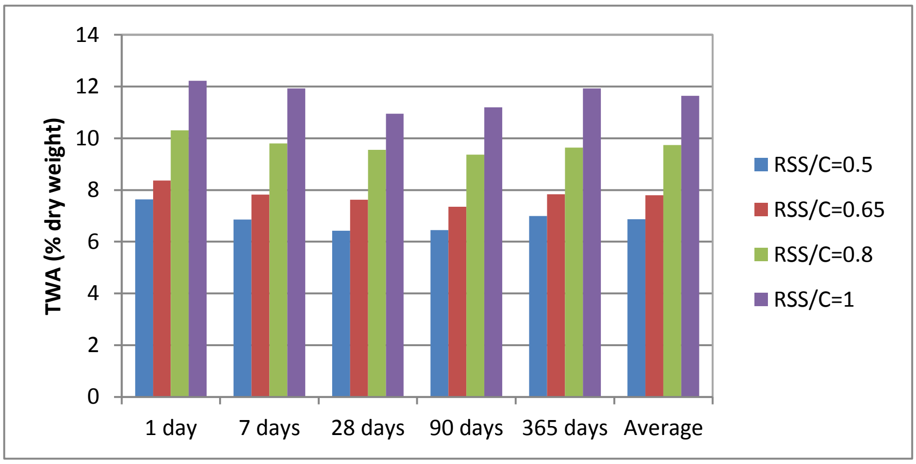


Figure 4.21: TWA for mortar mixes with different RSS content (Group 1).

Influence of sand content (Group 2)

TWA for mortar mixes with different sand content is shown in Figure 4.22. Four mixes, that contained a constant RSS/Cement ratio of 0.8 and four sand to cement ratios of 3, 4.5, 6 and 7.5 (for M5, M3, M6 and M7 respectively), were investigated. TWA was recorded for mortar specimens at 1, 7, 28, 90 and 365 days, and the average TWA was determined. The results showed that TWA generally decreased with age until 365 days for all mixes in this group. However a clear trend in TWA was observed, as TWA decreased when the sand content increased and the greatest average TWA of 12% was recorded for the mortar mix with sand to cement ratio of 3 (M5).

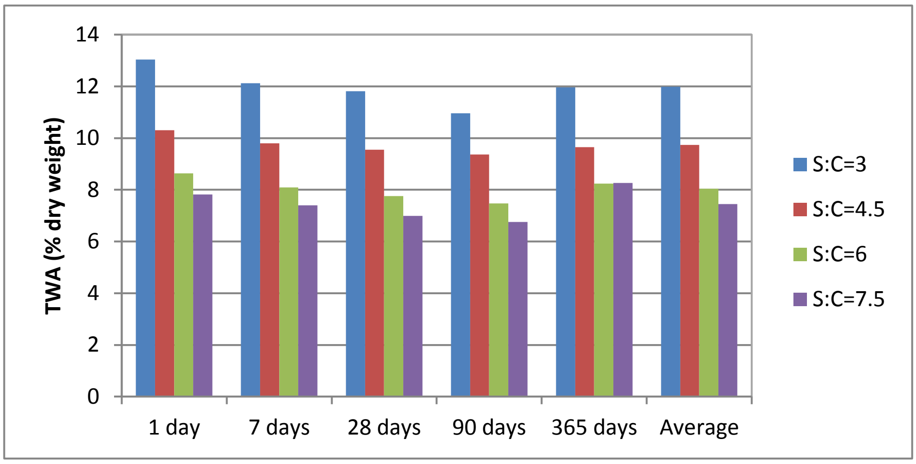


Figure 4.22: TWA for mortar mixes with diferent sand content (Group 2).

Influence of fly ash (Groups 3 and 4)

TWA for mortar mixes that incorporated RSS and different proportions of unprocessed fly ash is shown in Figure 4.23 and Figure 4.24. Two groups of mortar mixes that contained a constant sand to binder ratio of 4.5 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder), were examined. Group 3 (M2, M11, M12 and M13) was prepared with a RSS/Binder ratio of 0.65 whereas Group 4 (M3, M8, M9 and M10) was prepared with a RSS/Binder ratio of 0.8. TWA was recorded for mortar specimens at 1, 7, 28, 90 and 365 days, and the average TWA was determined. The results showed that TWA values were varying with curing age for all mixes, as TWA decreased with curing age until its subsequent rise at 365 days, except for M8. The results also showed that TWA for Group 3 increased steadily when unprocessed fly ash content increased and the greatest average TWA value of 9.1% was recorded for the mortar mix with 30% unprocessed fly ash (M13). For Group 4, the average results showed that replacing cement with unprocessed fly ash at 10% of total binder weight (M11) decreased TWA in comparison with the mix that contained 0% unprocessed fly ash replacement (M2). However, the addition of unprocessed fly ash increased TWA for both other mixes (M12 and M13). Additionally and in general, TWA increased when RSS content increased for all mixes with unprocessed fly ash.

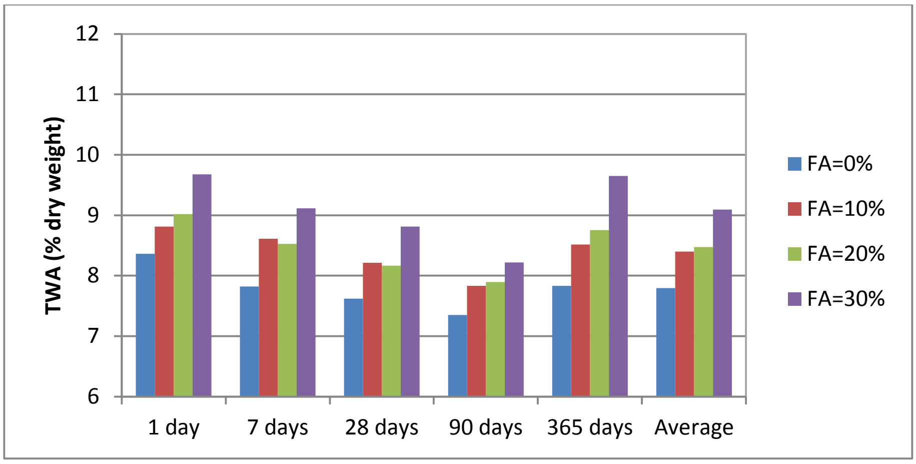


Figure 4.23: TWA of mortar mixes with different unprocessed fly ash replacement and RSS/Binder ratio of 0.65 (Group 3).

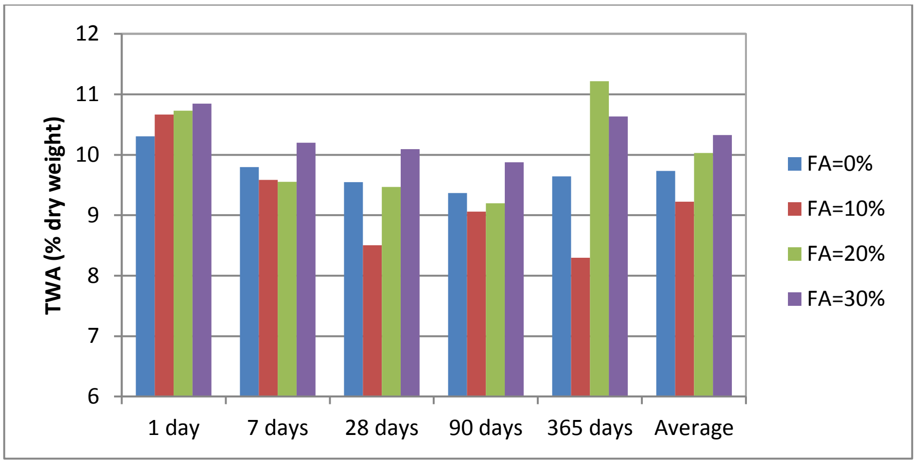


Figure 4.24: TWA of mortar mixes with different unprocessed fly ash replacement and RSS/Binder ratio of 0.8 (Group 4).

Influence of fly ash in the control (Group 5)

TWA of the control mixes is shown in Figure 4.25. This group of mixes (M14, M15, M16 and M17) contained a constant sand to cement ratio of 4.5, Water/Binder ratio of 0.8 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder). TWA was recorded for mortar specimens at 1, 7, 28, 90 and 365 days, and the average TWA was determined. The results generally showed that TWA varied with curing age for all mixes, as TWA decreased with age until its subsequent rise at 365 days. However, a clear trend in TWA values was observed, as it steadily increased when the unprocessed fly ash content increased and the greatest average TWA value of 11 % was recorded for the mortar mix with 30% unprocessed fly ash (M17).

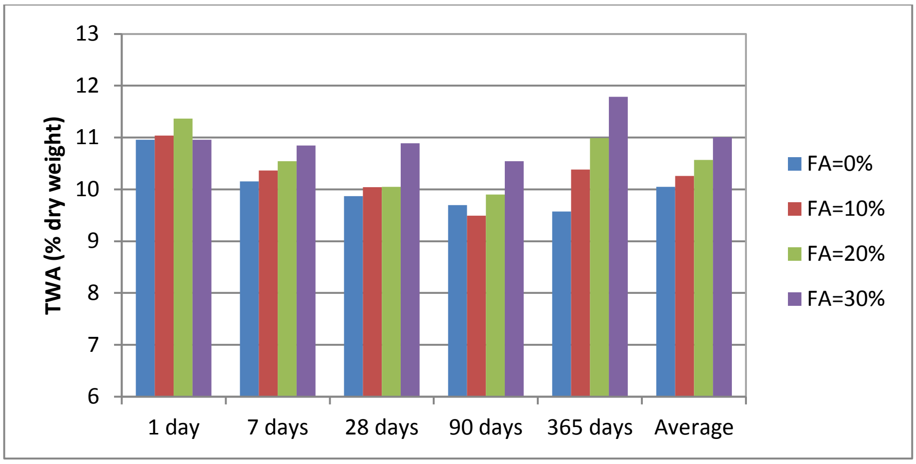


Figure 4.25: TWA of the control mixes with different unprocessed fly ash replacements and Water/Binder ratio of 0.8 (Group 5).

TWA of the mortar mixes with water and RSS is shown in Figure 4.26, and the relative TWA is presented in Table 4.12. Both show no significant differences in TWA between mixes contained RSS and those made with water. The relative TWA was ranged between 90.2-102.2%.

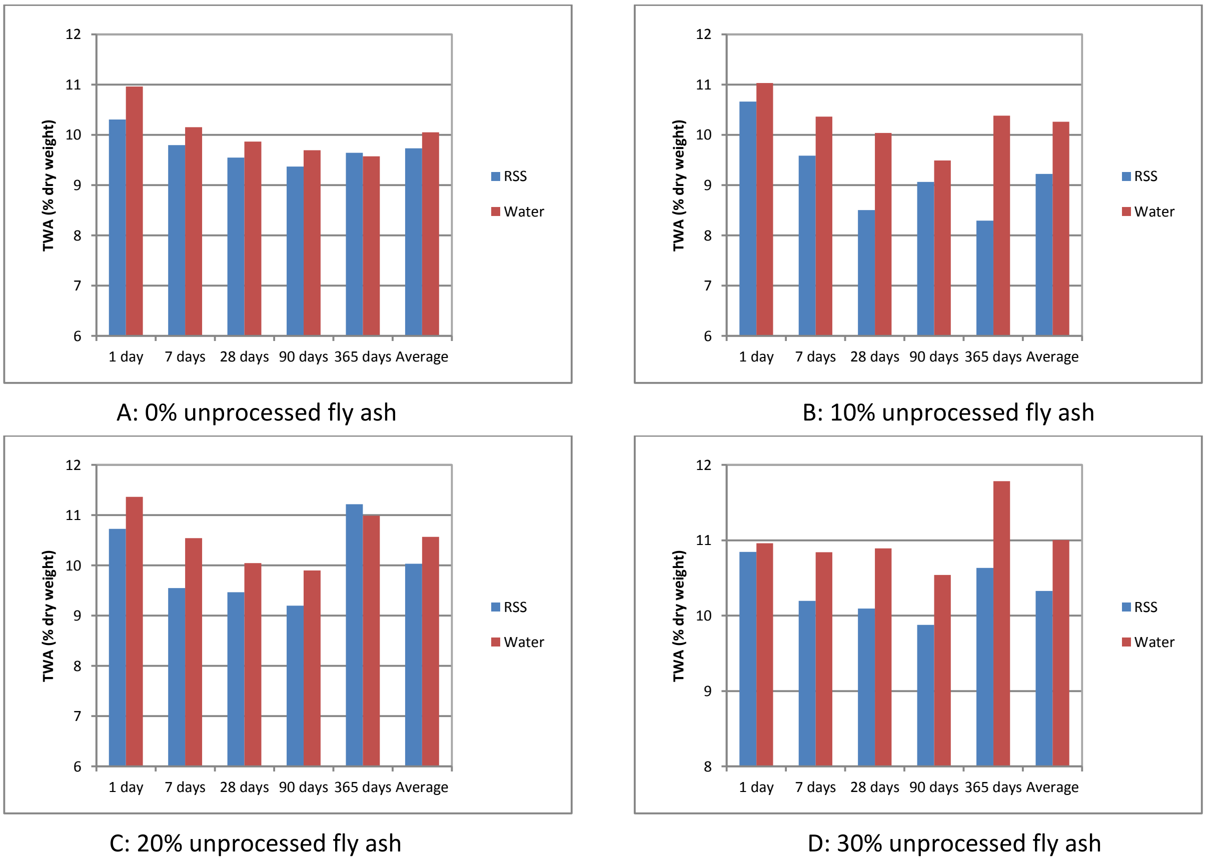


Figure 4.26: TWA of mortar mixes that contained both water and RSS.

Table 4.12: Relative TWA (%) of mortar mixes with RSS in comparison to those made with water.

Mixes	Fly ash %	Relative TWA (%)					
		1 day	7 days	28 days	90 days	365 days	Average
M3/M14	0	94.0	96.5	96.8	96.6	100.8	96.9
M8/M15	10	96.7	92.5	84.7	95.5	79.9	89.9
M9/M16	20	94.4	90.6	94.2	92.9	102.1	94.9
M10/M17	30	99.0	94.0	92.7	93.7	90.2	93.9

4.4.3.2 Series 2: Mortar mixes with large proportions of unprocessed fly ash

Table 4.13 and Figure 4.27 show the TWA of mortar specimens with large proportions of unprocessed fly ash. Four mixes, that contained a constant sand to cement ratio of 4.5 and a constant Water/Binder ratio of 1, were examined. One more mix that incorporated drinking water was also investigated and considered as the control. Cement was replaced with 0, 40, 60 and 80% unprocessed fly ash by weight of total binder. Samples were cured and tested for their TWA at 1, 7, 28, 90 and 180 days. The results showed that TWA varied with curing age for all mixes. The results also showed that the addition of unprocessed fly ash generally increased TWA and the greatest average TWA was recorded for the mortar mix with 80% unprocessed fly ash (ML4). No significant difference in TWA was observed between the control mix (MLRef) and that made with water (ML1) (Figure 4.28). The relative TWA ranged between 93-100.01% (Table 4.14).

Table 4.13: TWA of mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2).

Mix	Fly ash %	TWA (% dry weight)					
		1 day	7 days	28 days	90 days	180 days	Average
MLRef	0	13.9	14.9	12.3	12.0	11.5	12.9
ML1	0	13.8	14.2	12.4	11.8	10.7	12.6
ML2	40	13.8	13.8	13.6	12.9	12.1	13.2
ML3	60	ND	14.3	14.8	13.2	13.5	14.0
ML4	80	ND	16.2	16.5	15.7	14.5	15.7

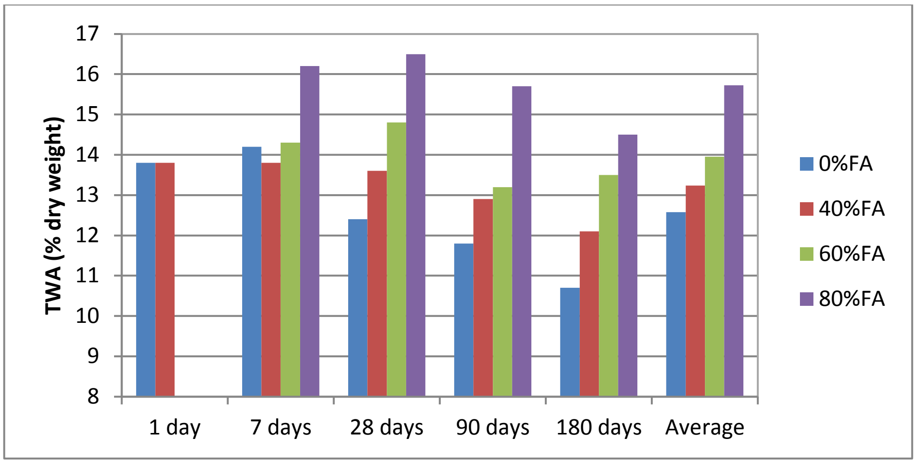


Figure 4.27: TWA of mortar mixes with RSS and large proportions of unprocessed fly ash (Series 3).

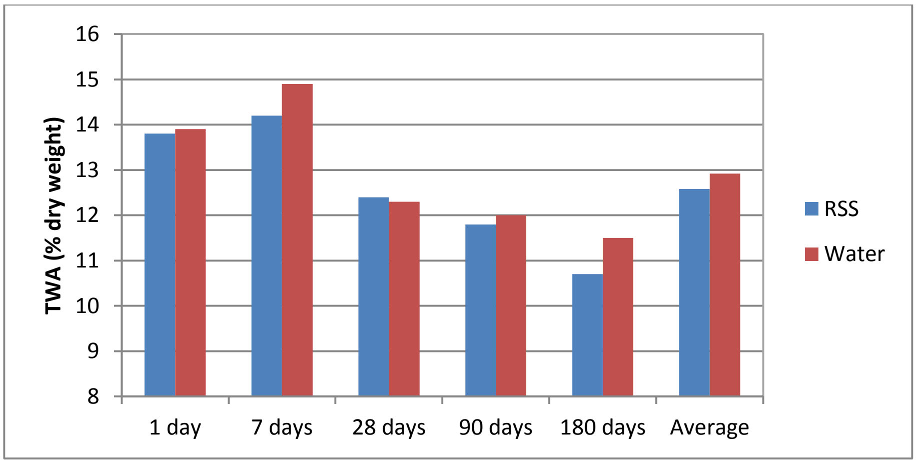


Figure 4.28: TWA of mortar mixes with RSS and water (Series 3).

Table 4.14: Relative TWA (%) of mortar mixes with RSS in comparison to those made with water (Series 2).

Mixes	Fly ash %	Relative TWA (%)					
		1 day	7 days	28 days	90 days	180 days	Average
ML1/MLRef	0	99.2	95.3	100.01	98.3	93	97.7

4.4.3.3 Series 3: Concrete mixes with RSS and unprocessed fly ash

TWA of the concrete mixes is shown in Table 4.15 and Figure 4.29. This series consisted of four mixes that incorporated a constant Cement:Sand:Gravel ratio of 1:1.5:3 respectively and Liquid/Binder ratio of 0.5. Cement was replaced with 0, 10, 15, 20% unprocessed fly ash by weight of total binder. One more concrete mix (CMRef), made of drinking water with

(Water/Cement ratio =0.5) was investigated and considered as the control. Concrete specimens were cured for 1, 7, 28, 90 and 300 days. The results showed no clear trend in TWA with curing age. However, the results showed that the average TWA increased when unprocessed fly ash content increased up to 15% replacement (MC3), where the highest average TWA value of 6.6% was recorded. The results also showed that TWA for the control mix was relatively higher than that with RSS, as the average TWA for CMRef was 6.5% and for CM1 was 6.1% (Figure 4.30 and Table 4.16).

Table 4.15 : TWA of concrete mixes with RSS and unprocessed fly ash (Series 3).

Mix	Fly ash %	TWA (% dry weight)					
		1 day	7 days	28 days	90 days	300 days	Average
CMRef	0	7.4	6.0	7.0	6.3	5.9	6.5
CM1	0	6.5	6.6	6.6	5.8	4.9	6.1
CM2	10	7.1	6.8	6.2	6.1	4.9	6.2
CM3	15	7.2	7.0	6.8	6.9	4.9	6.6
CM4	20	7.3	6.6	7.0	6.0	5.0	6.4

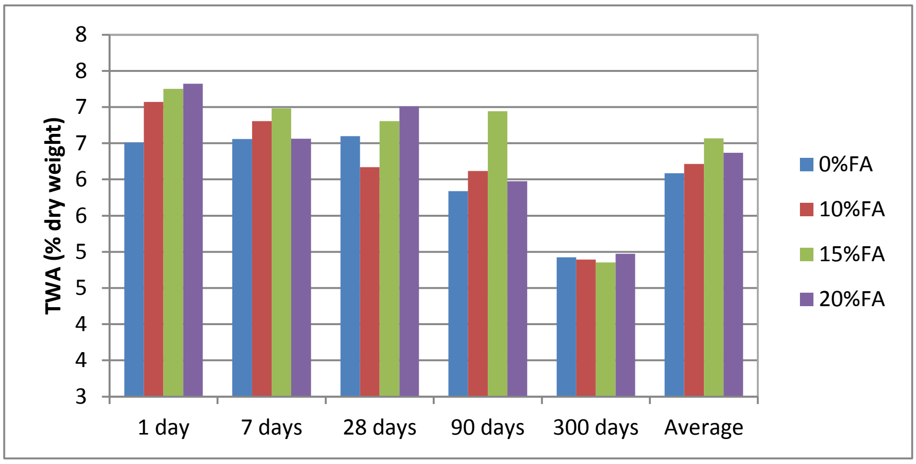


Figure 4.29: TWA of concrete mixes with RSS and unprocessed fly ash (Series 3).

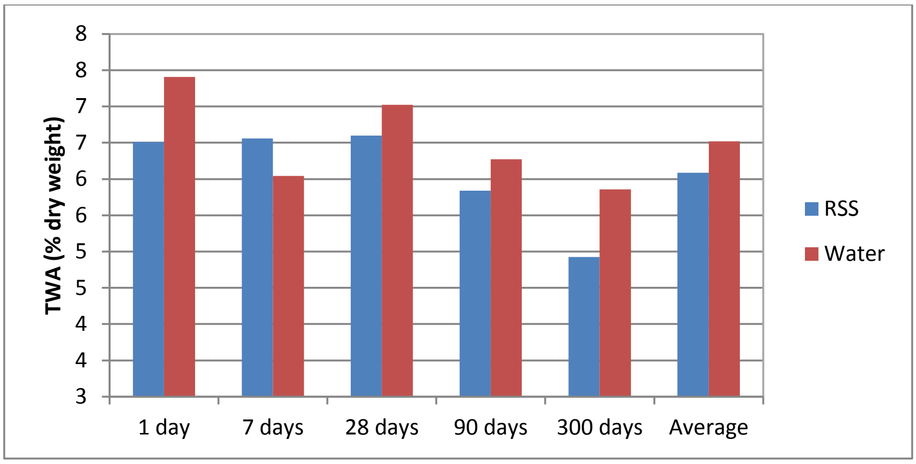


Figure 4.30: TWA of concrete mixes with RSS and water (Series 3).

Table 4.16: Relative TWA (%) of concrete mixes with RSS in comparison to those made with water (Series 3).

Mixes	Fly ash %	Relative TWA (%)					
		1 day	7 days	28 days	90 days	300 days	Average
CM1/CMRef	0	87.8	110	94.3	92.1	83.1	93.8

4.5 CONCLUSIONS

This chapter examined the physical properties of cement-based materials that incorporated RSS and unprocessed fly ash. Three series of cement-based materials were examined for their flowability/workability, density and TWA. Cement-based materials included mortar mixes with RSS and unprocessed fly ash, mortar mixes with RSS and large proportions of unprocessed fly ash, and concrete mixes with RSS and unprocessed fly ash. The main conclusions of this chapter are summarised below:

- **Flowability/Workability**
    - Group 1: Flowability of mortar mixes increased when the content of RSS increased and the greatest flowability value of 233mm was recorded for the mortar mix with RSS/Cement ratio of 1.
    - Group 2: Flowability of mortar mixes with RSS increased when the sand content reduced and the greatest value of 230mm was recorded for the mortar mix with sand to cement ratio of 3.
    - Groups 3 and 4: The addition of unprocessed fly ash significantly reduced flowability of the mortar mixes with both RSS and water. For Group 3, the reduction in flowability was 5.4, 11.5 and 17.7% for 10, 20 and 30% unprocessed

fly ash replacement respectively. For Group 4, the reduction in flowability due to the inclusion of unprocessed fly ash was 25.3, 30.9 and 36.5% for 10, 20 and 30% unprocessed fly ash replacement respectively.

- Group 5: For the control mixes (Group 5), the flowability was reduced by 23.1, 35.9 and 41% when cement was replaced with 10, 20 and 30% unprocessed fly ash respectively. The flowability of the mortar mixes with RSS was comparatively less than those with water. The flowability values of M3, M8, M9 and M10 (mortar mixes with RSS) were 9, 12, 2 and 2% less than that for M14, M15, M16 and M17 (mortar mixes with water) respectively.
- Series 2: Flowability of the mortar mixes that contained RSS was 20.8% less than that for the mix with water. The addition of unprocessed fly ash significantly reduced flowability. The reduction in flowability was 45.3, 57.9 and 57.9% for 40, 60 and 80% unprocessed fly ash replacement respectively.
- Series 3: Workability of the concrete mixes that contained RSS was 31.4% less than that for the mix with water. The workability of the concrete mixes was significantly reduced when unprocessed fly ash was included. The reduction in workability was 54.2, 90 and 95.8% for 10, 15 and 20% unprocessed fly ash replacement respectively.

- **<u>Density</u>**
  - Group 1: The average density of mortar mixes with RSS decreased when the content of RSS increased and the greatest average density of 2249 kg/m^3 was recorded for the mortar mix with RSS/Cement ratio of 0.5. Group 2: The average density steadily increased when the sand content increased up to sand to cement ratio of 6.
  - Groups 3 and 4: For the mortar mixes that contained unprocessed fly ash and RSS/Binder ratio of 0.65 (Group 3), the average density decreased when the content of unprocessed fly ash increased and the greatest average density of 2203 kg/m^3 was recorded for the mortar mix with 0% unprocessed fly ash (M2). For the mortar mixes with unprocessed fly ash and RSS/Binder ratio of 0.8 (Group 4), the average density steadily increased with the inclusion of unprocessed fly ash and the greatest average density of 2101 kg/m^3 was recorded for the mortar mix with 20% unprocessed fly ash (M9).
  - Group 5: For the control mixes (Group 5), the highest average density of 2161 kg/m^3 was recorded for the mix with 10% unprocessed fly ash (M15). The average density of the mortar mixes with RSS was comparatively less than those with water. The average density values of M3, M8, M9 and M10 (mortar mixes

with RSS) were 2.7, 3.5, 1.8 and 3.5% less than that for M14, M15, M16 and M17 (mortar mixes with water) respectively.

- Series 2: For the mortar mixes with large proportions of unprocessed fly ash, the average density of the mix that contained RSS (ML1) was 3.6% less than that made with water (MLRef). The results showed that the greatest average density of 2061 kg/m^3 was recorded for the mortar mix with 40% unprocessed fly ash replacement.
- Series 3: For the concrete mixes, the average density of the concrete mix that contained RSS (CM1) was 5.3% less than that for the control mix (CMRef). The results showed that the greatest average density of 2302 kg/m^3 was recorded for the concrete mix with 15% unprocessed fly ash (MC3).

- **Total Water Absorption (TWA)**
  - Group 1: TWA of mortar mixes increased when the content of RSS increased and the greatest average TWA value of 11.6% was recorded for the mortar mix with RSS/Cement ratio of 1.
  - Group 2: For mortar mixes with RSS and different sand content (Group 2), TWA decreased when the sand content increased and the greatest average TWA of 12% was recorded for the mix with sand to cement ratio of 3 (M5).
  - Groups 3 and 4: For the mortar mixes that contained unprocessed fly ash and RSS/Binder ratio of 0.65 (Group 3), the average TWA increased when the content of unprocessed fly ash increased and the greatest average TWA of 9.1% was recorded for the mortar mix with 30% unprocessed fly ash (M13). For the mortar mixes with unprocessed fly ash and RSS/Binder ratio of 0.8 (Group 4), the average TWA generally increased with the inclusion of unprocessed fly ash and the highest average TWA of 10.3% was recorded for the mortar mix with 30% unprocessed fly ash (M10).
  - Group 5: For the control mixes, the highest average TWA 11% was recorded for the mix with 30% unprocessed fly ash (M17). The TWA of the mortar mixes with RSS was comparatively less than those with water. The average TWA values of M3, M8, M9 and M10 (mortar mixes with RSS) were 3.1, 10.1, 5.1 and 6.1% less than that for M14, M15, M16 and M17 (mortar mixes with water) respectively.
  - Series 2: The addition of unprocessed fly ash generally increased the TWA values and the greatest average TWA of 15.7% was recorded for the mortar mix with 80% unprocessed fly ash (ML4). The average TWA for the mortar mix with RSS (ML1) was 2.3% less than that for the control mix (MLRef).

- Series 3: The average TWA increased when unprocessed fly ash content increased up to 15% replacement and the highest average TWA was 6.6%.
- The average TWA of the concrete mix with RSS (CM1) was 6.2% less than that for the control mix (CMRef).

CHAPTER 5: MECHANICAL PROPERTIES

5.1 INTRODUCTION

Strength of cement-based materials is commonly considered to be the most important property that can be used to determine the quality of concrete. Compressive strength is of a significant interest to structural engineers, such that their designs are much dependant of this property at 28 days. Nevertheless and despite the fact that compressive strength and its development with time is one of the most valuable properties; it is not the only property that is used to evaluate the quality of cement-based materials. Other important properties include volume stability (volume change), UPV and flexural strength.

Mechanical properties (strength, UPV and drying shrinkage) of cement-based materials are dependent on a number of interacting factors including water content, aggregate type and grading, aggregate/cement ratio, fineness of cement and also depends on other factors including presence of admixtures. The compaction degree along with water content and the grading of fine particles in concrete mixes contribute to the volume of voids in hardened concrete, as void in hardened concrete are either bubbles of entrapped air or spaces left after excess water has been evaporated. Thus the presence of voids in concrete reduces the density and consequently reduces compressive strength: 5% of voids can reduce the compressive strength by as much as 30% (Neville and Brooks, 2004).

The examination of the mechanical properties including UPV, compressive strength, flexural strength and drying shrinkage is a vital step to assess the possibility of utilising RSS and unprocessed fly ash in cement-based materials. UPV is an important parameter that can be indirectly used to assess strength related properties. Compressive strength is the most important parameter that can be used to evaluate the quality of used cement-based materials, whereas flexural strength is an indirect test to evaluate the influence of using RSS and unprocessed fly ash on tensile strength. The last parameter (drying shrinkage) is to assess the volume stability of used materials that are subjected to drying shrinkage.

5.2 AIMS AND OBJECTIVES

The aim of this chapter is to evaluate the mechanical properties of cement-based materials incorporating RSS and unprocessed fly ash. Three series of cement-based materials were examines. This included mortar mixes with RSS and unprocessed fly ash (Series 1), mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2), and concrete mixes with RSS and unprocessed fly ash (Series 3). This chapter will evaluate a number of mechanical properties including Ultrasonic Pulse Velocity (UPV), compressive strength, flexural strength, and drying shrinkage.

5.3 MATERIALS, MIXING PROPORTIONS, PREPARATIONS AND TESTING

The materials that were used throughout the experimental work included Portland cement, fine aggregate (sand), coarse aggregate (gravel), drinking water, Raw Sewage Sludge (RSS) and unprocessed fly ash. More details about used materials are available in Section 3.3.

Three series of cement-based mixes were tested for their mechanical properties including mortar mixes with RSS and unprocessed fly ash (Series 1), mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2), and concrete mixes with RSS and unprocessed fly ash (Series 3). Mechanical properties include Ultrasonic Pulse Velocity (UPV), compressive strength, flexural strength and length change. All groups in Series 1 were investigated; Group 2 was only tested for its UPV and compressive strength. Series 2 was also tested for its UPV and compressive strength only. The mixing proportions of the investigated series are described in more details in Section 3.3.10.

For the determination of ultrasonic pulse velocity and compressive strength, 50 mm in size specimens were used for mortar mixes, and 100 mm in size specimens for concrete samples. Mortar samples were prepared in accordance to ASTM C109/C109M-08 (ASTM, 2008). Concrete samples were prepared in accordance to BS EN 12390-3:2009 (BSI, 2009b). For the determination of flexural strength, 40x40x160 mm in size prisms that comply with BS EN 1015-11:1999 (BSI, 1999b) were used for mortar mixes. These prisms were also used to prepare mortar specimens for drying shrinkage. For the concrete mixes, 100x100x500 mm in size prisms that comply with BS EN 12390-5:2009 (BSI, 2009c) were used. Concrete specimens for drying shrinkage were prepared using 75x75x280 mm in size prisms that comply with the requirements of BS ISO 1920-8:2009 (BSI, 2009e). Cast specimens were covered with plastic sheets and placed in a room at a temperature of 20 ± 2^oC for 24 hours until demoulding. Thereafter, samples were wrapped by either a cling film (for mortar sampler) or plastic sheets (for concrete samples) until testing. More details about samples preparations are available in Section 3.4.

Ultrasonic pulse velocity is a traditional method used to examine the quality of construction materials, mainly concrete, by measuring the time requirements for an ultrasonic pulse to transmit through tested specimens. 50x50x50mm in size specimens were used for the determination of UPV for mortar mixes, and 100x100x100mm in size specimens were used for concrete mixes. Prior to crashing specimens for their compressive strength, ultrasonic pulse velocity was obtained using Proceq Pundit Lab+ instrument. Ultrasonic pulse velocity was calculated using Equation 3.4, and was recorded to the nearest 1m/sec (the average of three mortar specimen and two concrete specimens). Compressive strength for mortar mixes was determined using 50 mm in size cubes. The average compressive strength of three cubes was recorded to the nearest 0.1 N/mm^2. Mortar samples were tested in accordance to ASTM C109/C109M-08 (ASTM, 2008). For concrete samples, the average compressive strength of two cubes (100 mm in size) was recorded to the nearest 0.1 N/mm^2. Concrete cubes were tested in accordance to BS EN 12390-3:2009 (BSI, 2009b), with a loading rate of 0.6 MPa/sec. The compressive strength was obtained using Equation 3.5. Flexural strength for mortar mixes was determined using 40x40x160 mm in size prisms that comply with the requirements of BS EN 1015-11:1999 (BSI, 1999b). Flexural strength was obtained using SERCOMP7 hydraulic compressive strength machine with a loading rate of 50 N/sec. The average flexural strength of three prisms was calculated using Equation 3.6, and was recorded to the nearest 0.1 N/mm^2. For concrete mixes, 100x100x500 mm in size prisms that comply with BS EN 12390-5:2009 (BSI, 2009c) were used for flexural test. Flexural strength was obtained using SERCOMP7 hydraulic compressive strength machine with a loading rate of 50 N/sec. The average flexural strength of two prisms was calculated using Equation 3.6, and was recorded to the nearest 0.1 N/mm^2. Length change for mortar mixes was determined using 40x40x160 mm in size prisms, and 75x75x280 mm in size prisms that comply with the requirements of BS ISO 1920-8:2009 (BSI, 2009f) for concrete mixes. Two pairs of demec-studs were attached, at a distance of 100mm from each other, to the two sides of prism that were cast against the steel mould. Demec-studs were attached immediately after demoulding using super glue. Thereafter, prisms were placed in a room at a temperature of 21^{o}C $\pm$1^{o}C and a relative humidity of 50% $\pm$ 10%. Length change was monitored on a regular time intervals using a digital dial gauge that was measuring the length change between demec-studs on a single side. The reading of six sides for mortar specimens and four sides of concrete specimens were recorded to the nearest 0.001mm. Length change was obtained using Equation 3.7, and the average of three mortar prisms and two concrete prisms were recorded to the nearest 1 micro strain. More information about testing procedures is available in Sections 3.5.4, 3.5.5, 3.2.6 and 3.5.7.

5.4 RESULTS

5.4.1 Ultrasonic Pulse Velocity (UPV)

5.4.1.1 Series 1: Mortar mixes with RSS and unprocessed fly ash

The UPV results for this Series are presented in Table 5.1. The UPV results for each group in this Series are as follows:

Influence of RSS (Group 1)

Figure 5.1 shows the UPV values of mortar mixes with different RSS/Cement ratios. This group included four mortar mixes (M1, M2, M3 and M4) that incorporated a constant sand to cement ratio 4.5, 0% unprocessed fly ash and four RSS/Cement ratios of 0.5, 0.65, 0.8 and 1. For comparison purposes, M14 (which contained drinking water equivalent to the water content of M3), was also investigated. The figure clearly shows that UPV increased with the reduction of RSS content at all curing ages. The results also showed that the maximum UPV values were achieved at 90 days for all mixes except for the mortar mixes with RSS/Cement ratio of 0.5 (M1) and 1 (M4). UPV values for the control mix that was prepared with water (M14) were comparatively greater than those for the mix with RSS (M3) (Figure 5.6A).

Table 5.1: UPV for mortar mixes with RSS and unprocessed fly ash in m/s (Series 1).

Mix	UPV (m/s)				
	1 day	7 days	28 days	90 days	365 days
M1	3429	4144	4110	4104	3906
M2	3229	3769	3871	3896	3672
M3	2676	3444	3517	3542	3261
M4	2086	3018	3233	3219	3040
M5	2396	3202	3337	3282	3198
M6	2913	3542	3663	3745	3538
M7	2927	3517	3672	3656	3319
M8	2562	3362	3513	3529	3378
M9	2611	3268	3534	3555	3425
M10	2582	3151	3472	3542	3378
M11	3175	3676	3896	3861	3793
M12	3024	3584	3831	3846	3755
M13	2799	3521	3731	3686	3546
M14	3067	3550	3690	3708	3550
M15	2588	3432	3563	3764	3822
M16	2387	3240	3517	3812	3866
M17	2415	3254	3550	3764	3876

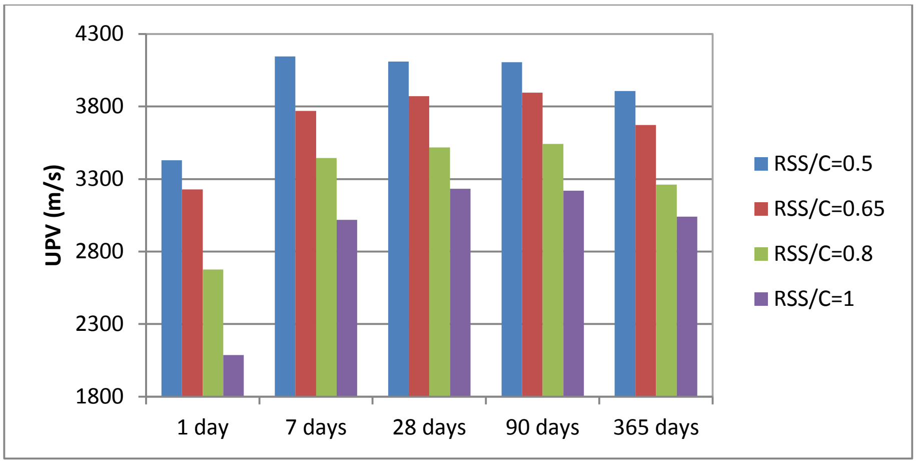


Figure 5.1 : UPV values of mortar mixes with different RSS content (Group 1).

Influence of sand content (Group 2)

The influence of varying sand content on UPV of mortar mixes is shown in Figure 5.2. Four mixes, that contained a constant RSS/Cement ratio of 0.8 and four sand to cement ratios of 3, 4.5, 6 and 7.5, were investigated. The results generally showed that the UPV values increased when the sand content increased up to a sand to cement ratio of 6 and the greatest UPV values were achieved at either 28 days or 90 days. UPV values declined at 365 days for all mixes in this group.

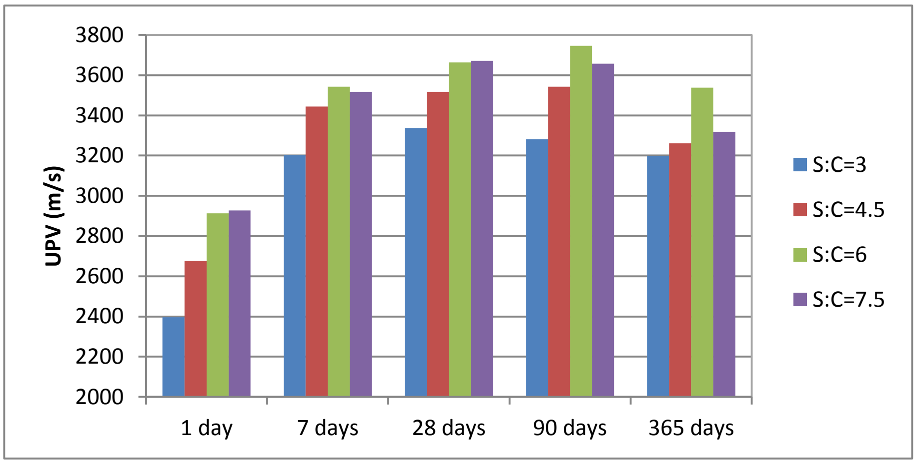


Figure 5.2 : UPV of mortar mixes with different sand to cement ratios (Group 2).

Influence of fly ash (Groups 3 and 4)

UPV of mortar mixes with RSS and different proportions of unprocessed fly ash is shown in Figure 5.3 and Figure 5.4. Two groups of mortar mixes that contained a constant sand to binder ratio of 4.5 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder), were examined. Group 3 (M2, M11, M12 and M13) was prepared with a

RSS/Binder ratio of 0.65 whereas Group 4 (M3, M8, M9 and M10) was prepared with a RSS/Binder ratio of 0.8. Figure 5.3 presents that UPV values decreased when the content of unprocessed fly ash increased at all curing ages in this group except for the mix with 10% unprocessed fly ash (M11) at 28 days. The maximum UPV values were achieved at either 90 days (M2: 0% unprocessed fly ash and M12: 20% unprocessed fly ash) or at 28 days (M11: 10% unprocessed fly ash and M13: 30% unprocessed fly ash). The figure also shows that UPV values declined at 365 days for all mixes in this group. Figure 5.4 shows that UPV values at earlier ages (1 and 7 days) generally decreased when the content of unprocessed fly ash increased. At later ages (28 and 90 days) no significant differences in UPV was observed, but more improvement in the UPV was observed at 365 days when unprocessed fly ash was increased up to 20% replacement (M9). Additionally, both Figure 5.3 and Figure 5.4 showed that UPV increased when the content of RSS reduced, as the UPV values for Group 3 were comparatively greater than those for Group 4.

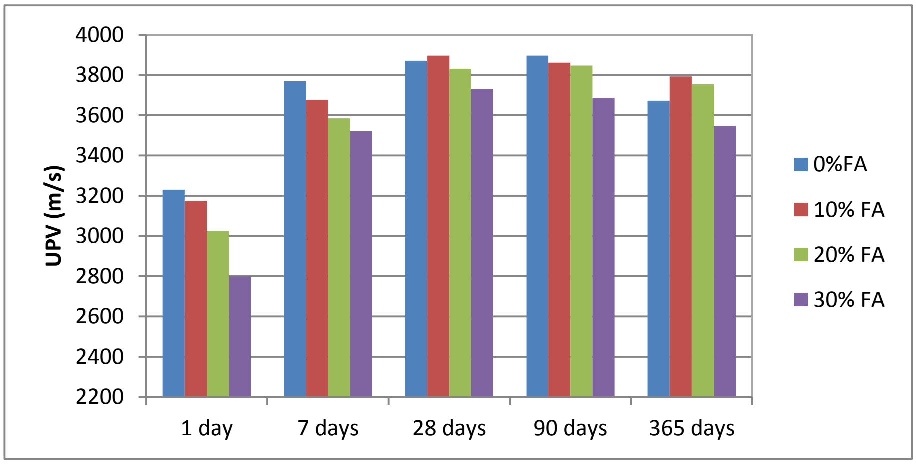


Figure 5.3 : UPV of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3).

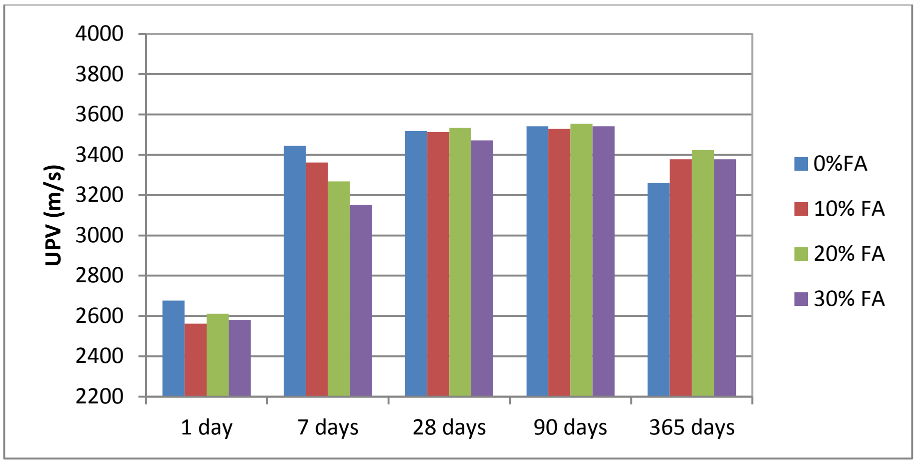


Figure 5.4 : UPV of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4).

Influence of fly ash in the control (Group 5)

UPV of the control mixes is shown in Figure 5.5. This group of mixes (M14, M15, M16 and M17) contained a constant sand to binder ratio of 4.5, Water/Binder ratio of 0.8 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder). The figure shows that UPV values at 1, 7 and 28 days decreased when unprocessed fly ash content increased and the greatest UPV readings were recorded for the mix with 0% unprocessed fly ash (M14). At later ages (90 and 365 days), the UPV values for mortar mixes with unprocessed fly ash were comparatively greater than those for the mix without it, and the greatest UPV values were recorded at 365 days. The results also showed that UPV values continued to improve with time until 365 days except for the mix with 0% unprocessed fly ash (M14).

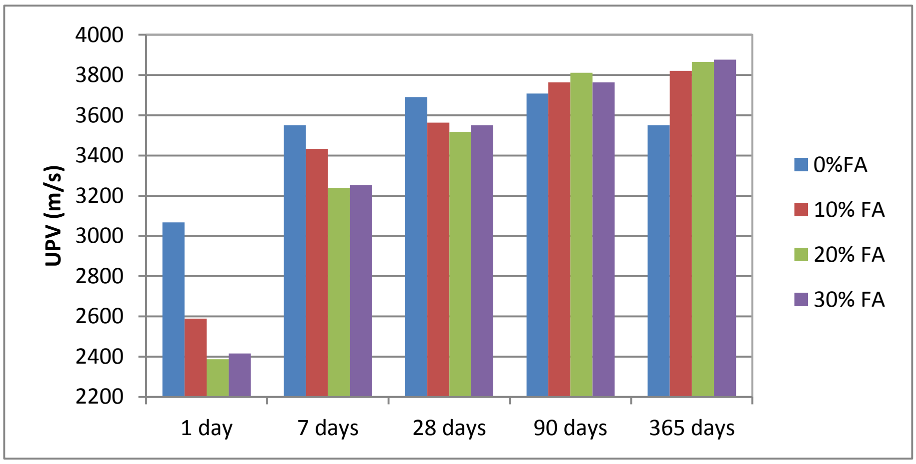
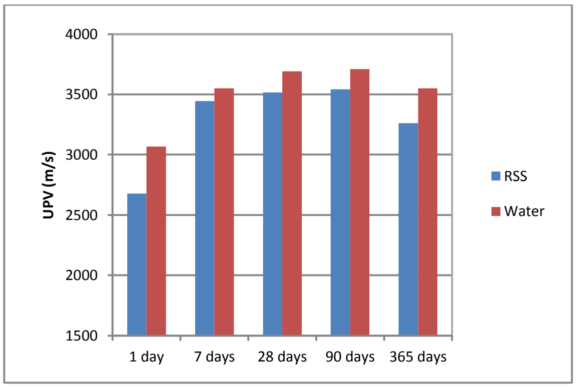
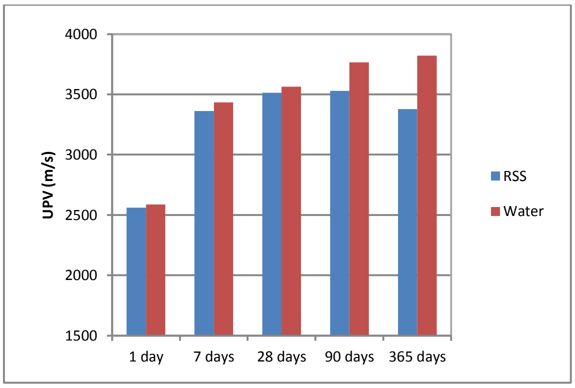


Figure 5.5 : UPV of control mixes with different unprocessed fly ash replacements and Water/Binder ratio of 0.8 (Group 5).

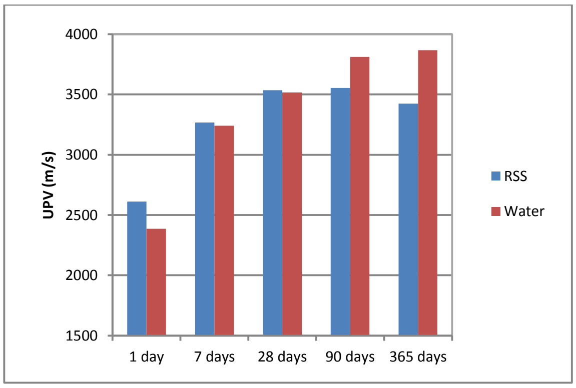
UPV of the mortar mixes with both water and RSS is shown in Figure 5.6, and the relative UPV of the mortar mixes with RSS in comparison to those with water is shown in Table 5.2. Both show that UPV values of the mortar mixes with water were generally higher than that of the mixes with RSS (except at 1 day for the mixes with 20 and 30%) and the relative UPV values ranged between 87.2-109.7% at 1 day, 96.8-100.9% at 7 days, 95.3-100.5% at 28 days, 93.2-95.5% at 90 days, and 88.4-91.8% at 365 days.



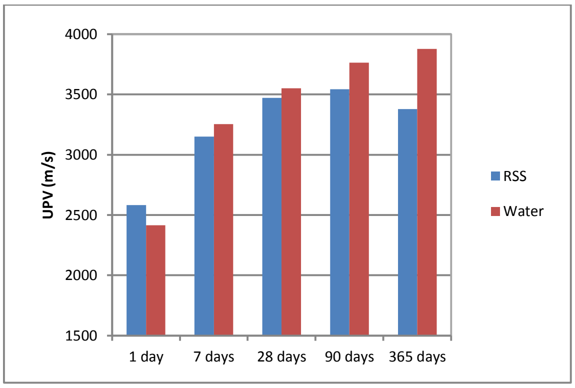
A: 0% unprocessed fly ash



B: 10% unprocessed fly ash



C: 20% unprocessed fly ash



D: 30% unprocessed fly ash

Figure 5.6: UPV of mortar mixes with both water and RSS.

Table 5.2: Relative UPV (%) of mortar mixes with RSS in comparison to those made with water.

Mixes	Fly ash %	Relative UPV (%)				
		1 day	7 days	28 days	90 days	365 days
M3/M14	0	87.2	97.0	95.3	95.5	91.8
M8/M15	10	99.0	97.9	98.6	93.8	88.4
M9/M16	20	109.4	100.9	100.5	93.2	88.6
M10/M17	30	106.9	96.8	97.8	94.1	87.2

5.4.1.2 Series 2: Mortar mixes with RSS and large proportions of unprocessed fly ash

The UPV of this series is presented in Figure 5.7 and Table 5.3. Four mixes, that contained a constant sand to binder ratio of 4.5 and Water:Binder ratio of 1, were examined. One more mix that contained drinking water was also investigated and considered as the control. Cement was replaced with 0, 40, 60 and 80% unprocessed fly ash by weight of total binder. Specimens were tested for their UPV at 1, 7, 28, 90 and 180 days. Figure 5.7 demonstrated that UPV generally decreased when unprocessed fly ash content increased and this can be clearly seen in all mixes of this series. However some improvement in UPV was observed for the mortar mix with 40% unprocessed fly ash (ML2) at 1, 7 and 180 days. The results also showed that UPV values of the control mix were comparatively greater than those for the mix with RSS (Figure 5.8), and the relative UPV values ranged between 84.4-100.5% (Table 5.4).

Table 5.3: UPV of mortar mixes with RSS and large proportions of unprocessed fly ash in m/s (Series 2).

Mix	Fly ash %	UPV (m/s)				
		1 day	7 days	28 days	90 days	180 days
MLRef	0	3200	3200	3650	3600	3580
ML1	0	2700	3030	3472	3595	3597
ML2	40	2800	3198	3378	3448	3606
ML3	60	ND	2651	3170	3261	3268
ML4	80	ND	1618	2270	2250	2160

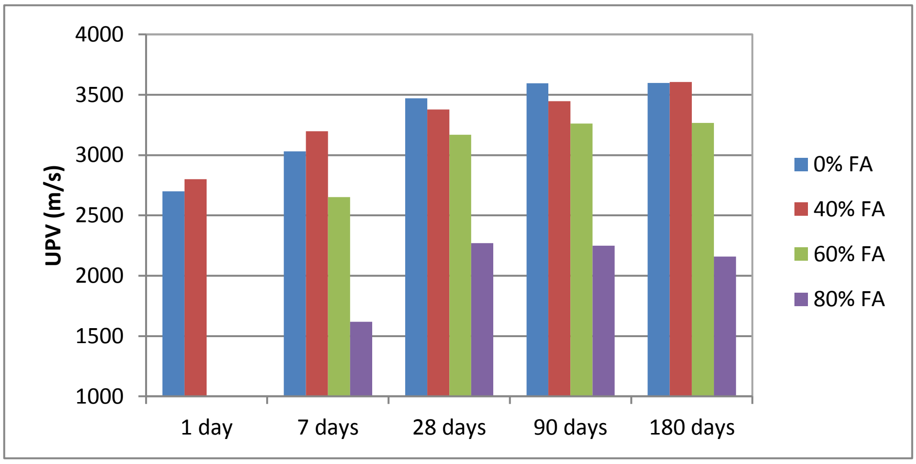


Figure 5.7: UPV of mortar mixes with RSS and large proportion of unprocessed fly ash (Series 2).

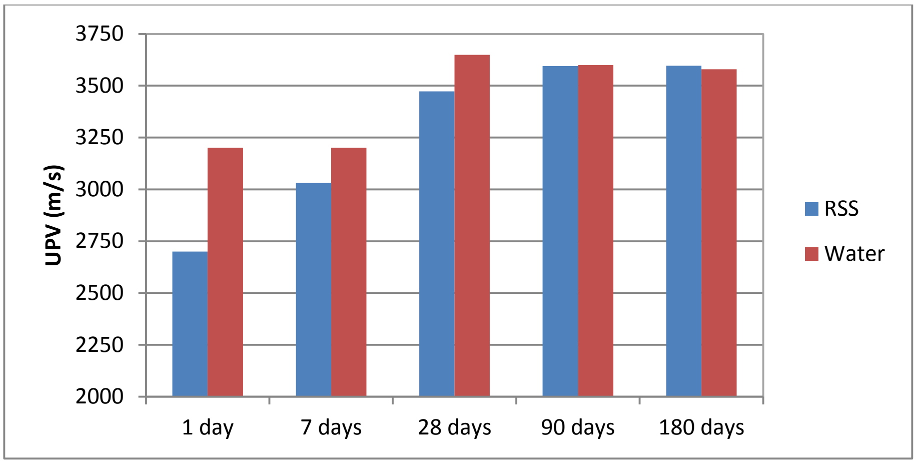


Figure 5.8: UPV of mortar mixes with RSS and water (Series 2).

Table 5.4: Relative UPV of the mortar mixes with RSS in comparison to those made with water (Series 2).

Mixes	Fly ash %	Relative UPV (%)				
		1 day	7 days	28 days	90 days	180 days
ML1/MLRef	0	84.4	94.7	95.1	99.9	100.5

5.4.1.3 Series 3: Concrete mixes with RSS and unprocessed fly ash

UPV values of the concrete mixes are shown in Table 5.5 and Figure 5.9. This Series consisted of four mixes that incorporated a constant cement:sand:gravel ratio of 1:1.5:3 respectively and Liquid/Binder ratio of 0.5. Cement was replaced with 0, 10, 15, and 20% unprocessed fly ash by weight of total binder. One more concrete mix (CMRef), made with drinking water (Water/Binder ratio=0.5) was investigated and considered as the control. Concrete specimens were tested for their UPV at 1, 7, 28, 90 and 300 days. Figure 5.9 shows that the addition of unprocessed fly ash did not significantly influence UPV at all curing ages except at 1 day. The results also showed that UPV values of the control mix were comparatively greater than those for the mix with RSS (Figure 5.10), and the relative UPV ranged between 93.7-97.3% (Table 5.6).

Table 5.5: UPV of concrete mixes with RSS and unprocessed fly ash in m/s (Series 3)

Mix	UPV (m/s)				
	1 day	7 days	28 days	90 days	300 days
CMRef	4246	4592	4756	4706	4773
CM1	4082	4306	4459	4530	4646
CM2	3854	4251	4430	4454	4582
CM3	3693	4338	4367	4348	4608
CM4	3731	4278	4386	4484	4592

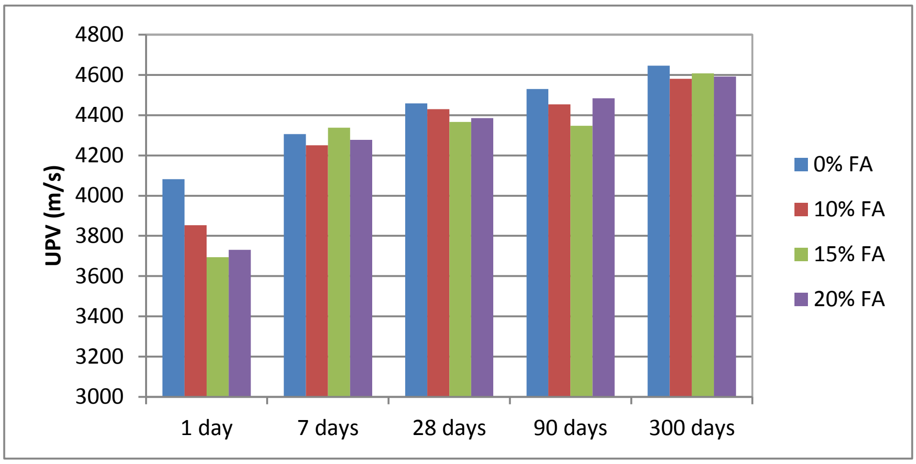


Figure 5.9: UPV of concrete mixes with RSS and unprocessed fly ash in m/s (Series 3).

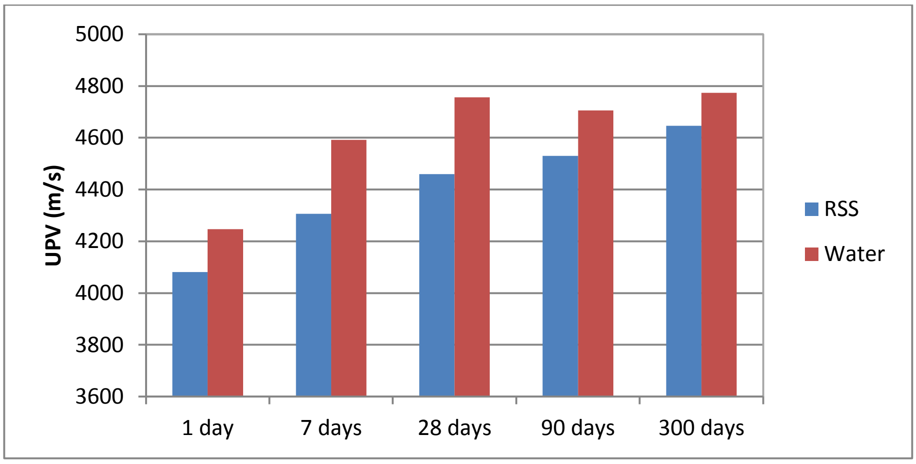


Figure 5.10: UPV of concrete mixes with RSS and water (Series 3).

Table 5.6: Relative UPV of concrete mixes with RSS in comparison to those made with water (Series 3).

Mixes	Fly ash %	Relative UPV (%)				
		1 day	7 days	28 days	90 days	300 days
CM1/CMRef	0	96.1	93.8	93.7	96.3	97.3

5.4.2 Compressive Strength

5.4.2.1 Series 1: Mortar mixes with RSS and unprocessed fly ash

The compressive strength of this series is presented in Table 5.7. The compressive strength results for each group in this series are as follows:

Influence of RSS (Group 1)

The compressive strength of the mortar mixes with different RSS content is presented in Figure 5.11. This group of mixes (M1, M2, M3 and M4) incorporated a constant sand to cement ratio 4.5, 0% unprocessed fly ash and four RSS/Cement ratios of 0.5, 0.65, 0.8 and 1. For comparison purposes, M14 (which contained drinking water equivalent to the water content of M3) was also investigated as the control. Mortar specimens were tested for their compressive strength at 1, 7, 28, 90 and 365 days. The figure shows a clear trend in the compressive strength with RSS content, as strength decreased when RSS content increased and the greatest compressive strength was achieved for the mortar mix with RSS/Cement ratio of 0.5 (M1). The results also showed that the compressive strength sustainably developed with curing age up to 90 days prior to its subsequent insignificant falling at 365 days (except for M3). Moreover, compressive strength of the mortar mix with RSS (M3) was fairly good in comparison with the mix that contained drinking water (M14), and the relative strength ranged between 56-70% (Figure 5.16A and Table 5.8).

Table 5.7: Compressive strength of mortar mixes with RSS and unprocessed fly ash in MPa (Series 1).

Mix	Compressive strength (MPa)				
	1 day	7 days	28 days	90 days	365 days
M1	10.7	26.7	36.0	43.7	35.7
M2	5.3	16.5	21.8	30.6	27.5
M3	2.1	8.1	11.8	18.7	17.9
M4	1.1	5.2	8.3	12.3	12.3
M5	2.3	11.0	15.5	20.5	22.2
M6	2.5	10.2	14.7	21.6	17.6
M7	3.6	8.6	14.4	19.1	15.4
M8	2.0	8.0	13.7	19.6	19.9
M9	2.0	7.7	13.5	19.3	19.8
M10	2.1	6.5	11.6	16.7	19.3
M11	4.6	13.9	19.9	27.2	27.9
M12	4.0	11.9	19.9	28.9	29.2
M13	4.1	10.9	17.0	23.6	24.4
M14	3.8	13.2	19.8	25.2	25.5
M15	2.5	10.7	15.3	19.7	26.4
M16	2.1	8.3	12.8	22.0	25.5
M17	2.1	7.4	11.8	20.2	25.8

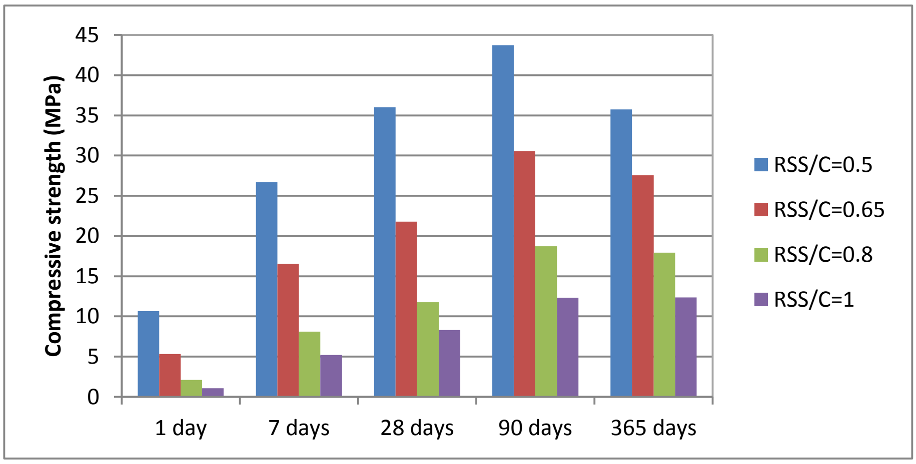


Figure 5.11: Compressive strength of mortar mixes with different RSS content (Group 1).

Influence of sand content (Group 2)

The influence of varying sand content on the compressive strength is shown in Figure 5.12. This group consisted of four mixes that contained a constant RSS/Cement ratio of 0.8 and four sand to cement ratios of 3, 4.5, 6 and 7.5 (M5, M3, M6 and M7 respectively). The results showed that the compressive strength at 7, 28, 90 and 365 days generally reduced when the sand content increased and the greater compressive strength was achieve for the mortar mix with sand to cement ratio of 3 (M5), except at 90 days for M6 (sand to cement ratio of 6). At early age, specifically 1 day, the compressive strength increased when the sand content increased. Moreover, the results showed that the compressive strength sustainably developed with curing age until 90 days prior to its subsequent insignificant falling at 365 days (except for M3: sand to cement ratio of 4.5).

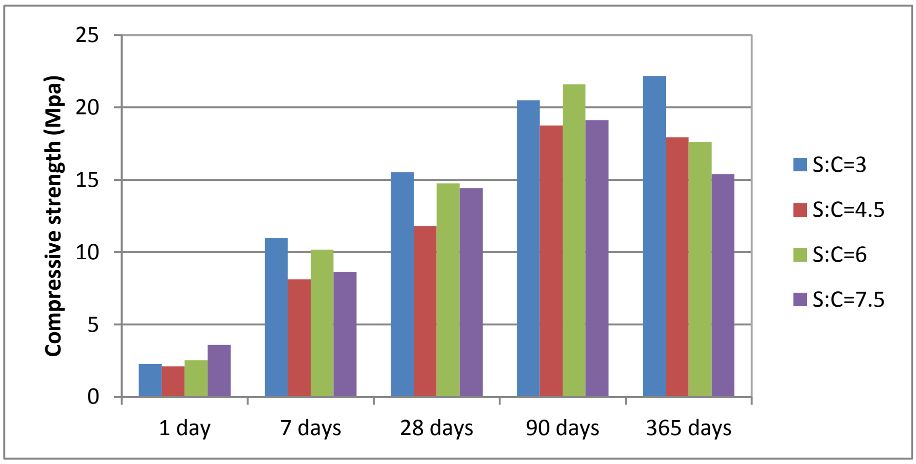


Figure 5.12: Compressive strength of mortar mixes with different sand content (Group 2).

Influence of fly ash (Groups 3 and 4)

Compressive strength of the mortar mixes with RSS and different proportions of unprocessed fly ash is shown in Figure 5.13 and Figure 5.14. Two groups of mortar mixes that contained a constant sand to binder ratio of 4.5 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder), were examined. Group 3 (M2, M11, M12 and M13) was prepared with a RSS/Binder ratio of 0.65 whilst Group 4 (M3, M8, M9 and M10) was prepared with a RSS/Binder ratio of 0.8. Figure 5.13 shows that compressive strength at early ages (1, 7 and 28 days) generally decreased when unprocessed fly ash content increased. At later ages (90 and 365 days) certain improvement in compressive strength was observed when the cement was replaced with unprocessed fly ash at 20% (except at 90 days for the mortar mix with 0% unprocessed fly ash). Figure 5.14 shows that the compressive strength of mortar mixes with unprocessed fly ash and RSS/Binder ratio of 0.8 increased when the content of unprocessed fly ash increased, and the greatest compressive strength values were achieved for the mortar mixes with 10 and 20% unprocessed fly ash replacement (M8 and M9 respectively). Moreover, the results showed that the addition of unprocessed fly ash improved long-term strength development, and prevented the decline of compressive strength observed in all mixes with RSS only at 365 days.

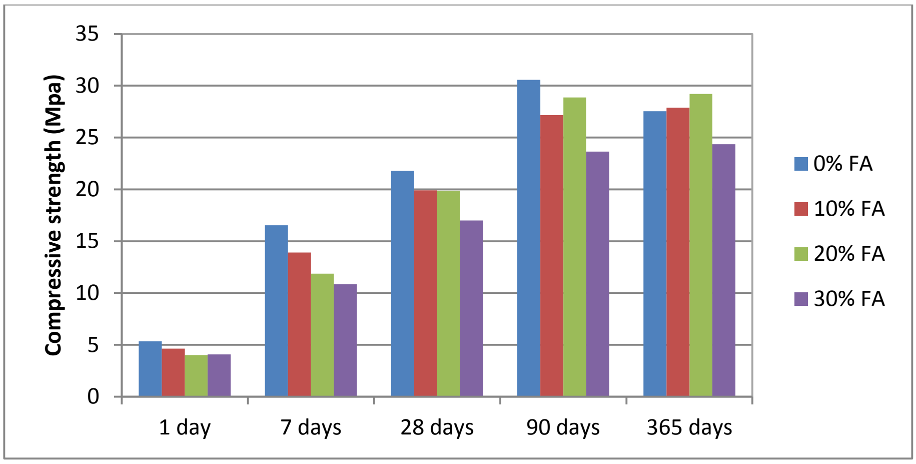


Figure 5.13: Compressive strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3).

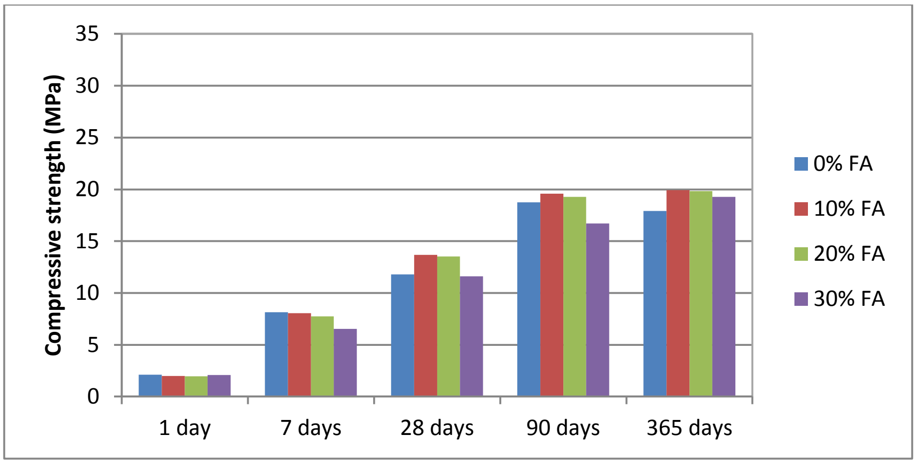


Figure 5.14: Compressive strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4).

Influence of fly ash in the control (Group 5)

Compressive strength of the control mixes is shown in Figure 5.15. This group of mixes (M14, M15, M16 and M17) contained a constant sand to binder ratio of 4.5, Water/Binder ratio of 0.8 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder). The results presented that the compressive strength at 1, 7, 28 and 90 days decreased when unprocessed fly ash content increased, and the greatest compressive strength was achieved for the mortar mix with 0% unprocessed fly ash (M14). At 365 days the results showed a noticeable improvement in the compressive strength for all mixes that contained unprocessed fly ash, and the greatest compressive strength of 26.4 MPa was recorded for the mortar mix with 10% unprocessed fly ash (M15).

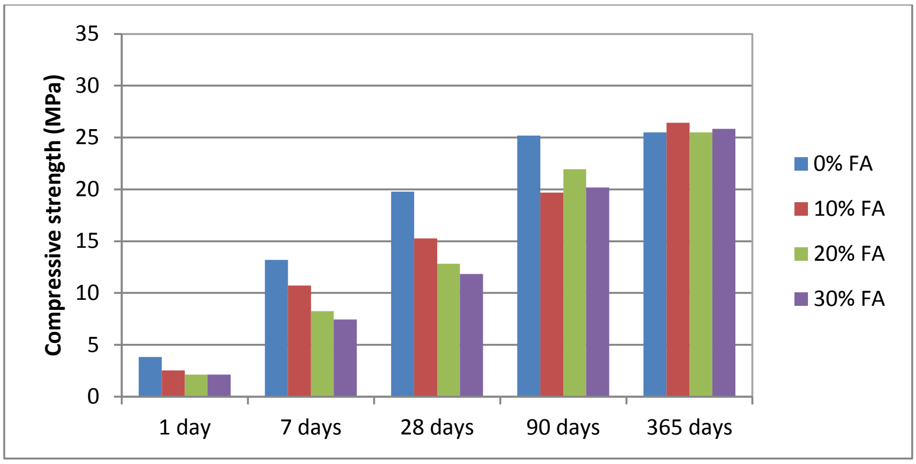


Figure 5.15: Compressive strength of control mixes with different unprocessed fly ash content and Water/Binder ratio of 0.8 (Group 5).

The compressive strength of the mortar mixes with water and RSS is shown in Figure 5.16, and the relative compressive strength of the mortar mixes made with RSS in comparison to those made with water is shown in Table 5.8. The compressive strength of the specimens that contained RSS was noticeably less than that of the mixes with water, and the relative compressive strength ranged between 56-97% at 1 day, 62-94% at 7 days, 60-105% at 28 days, 74-99% at 90 days, and 70-78% at 365 days.

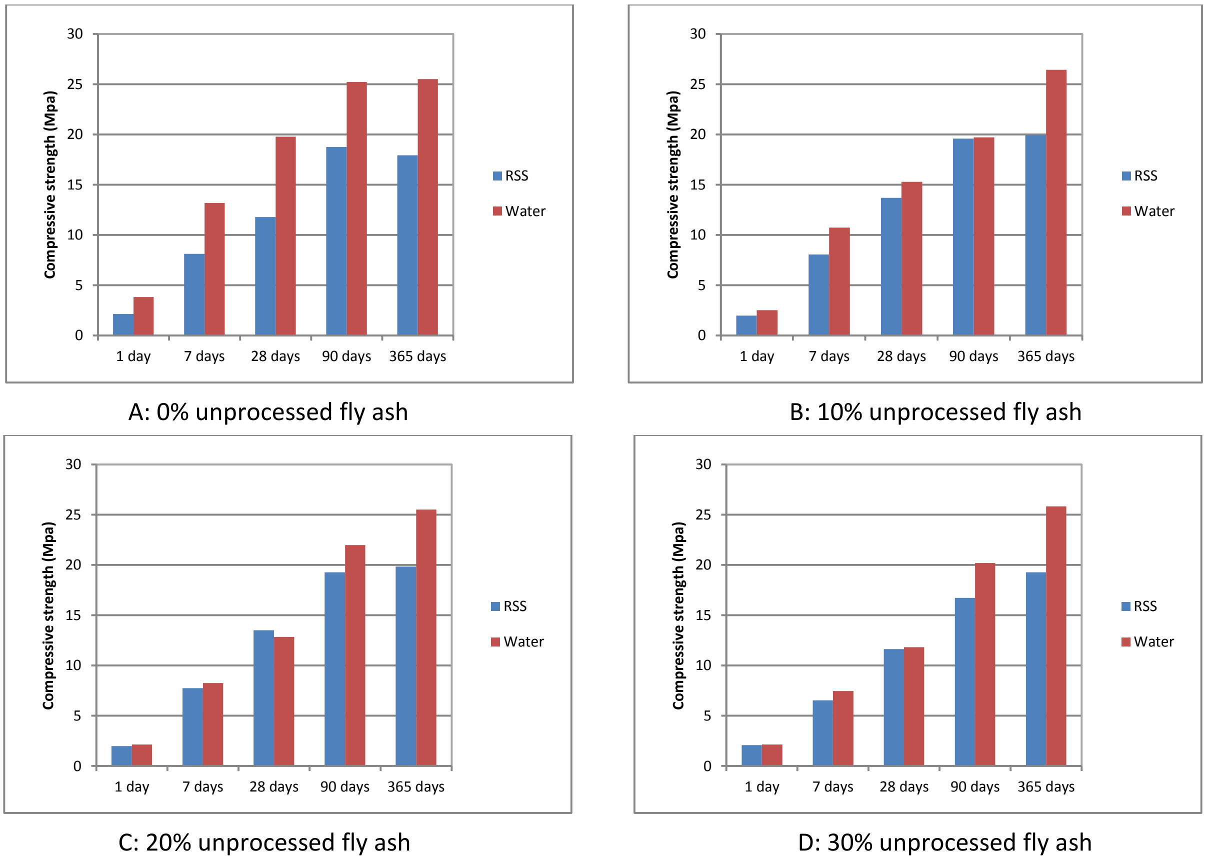


Figure 5.16: Compressive strength of mortar mixes with water and RSS.

Table 5.8: Relative compressive strength (%) of mortar mixes with RSS in comparison to those made with water.

Mixes	Fly ash %	Relative compressive strength (%)				
		1 day	7 days	28 days	90 days	365 days
M3/M14	0	56	62	60	74	70
M8/M15	10	79	75	90	99	75
M9/M16	20	93	94	105	88	78
M10/M17	30	97	88	98	83	75

5.4.2.2 Series 2: Mortar mixes with RSS and large proportions of unprocessed fly ash

The compressive strength of this series is presented in Table 5.9 and Figure 5.17. This series consisted of four mixes that contained a constant sand to binder ratio of 4.5 and Water/Binder ratio of 1. One more mix that incorporated drinking water was also investigated and considered as the control. Cement was replaced with 0, 40, 60 and 80% unprocessed fly ash by weight of total binder. Samples were tested for their compressive strength at 1, 7, 28, 90 and 180 days. The results showed that the compressive strength increased when unprocessed fly ash content was decreased at all ages. The results also demonstrated that the compressive strength of the control mix was comparatively greater than that contained RSS (Figure 5.18). The relative compressive strength values of ML1/MLRef ranged between 86.3-95.2% (Table 5.10).

Table 5.9: Compressive strength of mortar mixes with RSS and large proportions of unprocessed fly ash in MPa (Series 2).

Mix	Fly ash %	Compressive strength (MPa)				
		1 day	7 days	28 days	90 days	180 days
MLRef	0	1.3	9.0	13.4	16.8	18.6
ML1	0	1.2	8.2	11.6	15.2	17.1
ML2	40	1.1	4.0	6.3	10.7	12.5
ML3	60	ND	1.6	4.0	7.5	10.0
ML4	80	ND	0.6	1.4	1.9	2.1

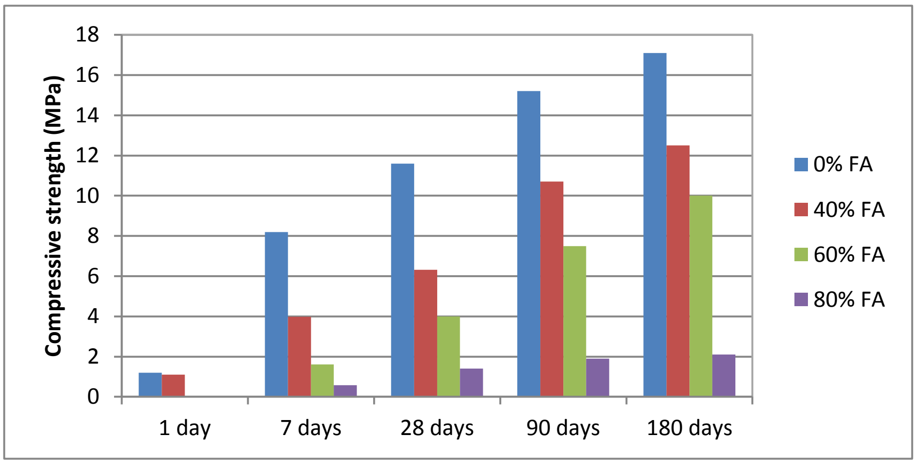


Figure 5.17: Compressive strength of mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2).

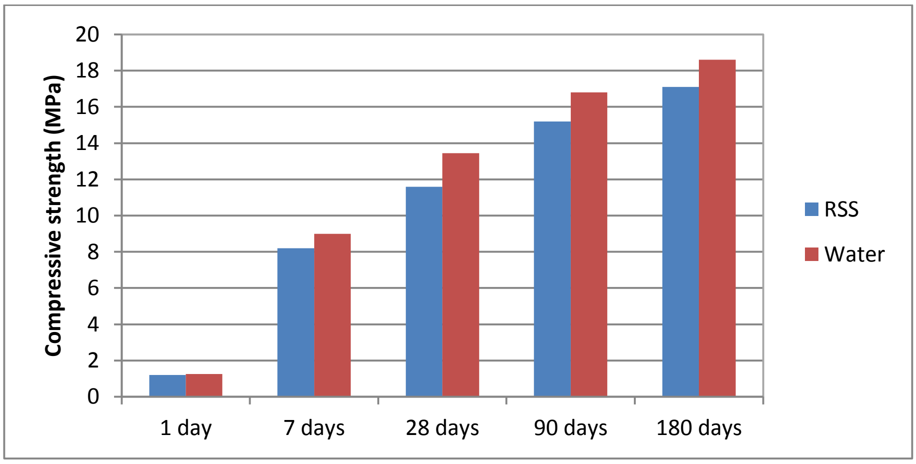


Figure 5.18: Compressive strength of mortar mixes with RSS and water (Series 2).

Table 5.10: Relative compressive strength of mortar mixes with RSS in comparison to those made with water (Series 2).

Mixes	Fly ash %	Relative compressive strength (%)				
		1 day	7 days	28 days	90 days	180 days
ML1/MLRef	0	95.2	91.1	86.3	90.5	91.9

5.4.2.3 Series 3: Concrete mixes with RSS and unprocessed fly ash

The compressive strength of this series is shown in Table 5.11 and Figure 5.19. This series included four concrete mixes that incorporated a constant cement:sand:gravel ratio of 1:1.5:3 respectively and Liquid/Binder ratio of 0.5. Cement was replaced with 0, 10, 15, and 20% unprocessed fly ash by weight of total binder. One more mix (CMRef) with drinking water was also investigated and considered as the control. Specimens were tested for their compressive strength at 1, 7, 28, 90 and 300 days. Figure 5.19 shows that the compressive strength at 1 day generally decreased when unprocessed fly ash content increased. The addition of 10% unprocessed fly ash improved compressive strength at 7 days. At 28 days, certain improvement in compressive strength was observed when cement was replaced with unprocessed fly ash at 10-20%. At 90 and 300 days, the compressive strength of the concrete mixes that contained 15% unprocessed fly ash showed a significant improvement in comparison to those with 0 and 10%. Moreover, the compressive strength of concrete mix that contained water was greater than that for the mix with RSS. The relative compressive strength values of CM1/CMRef ranged between 56-90% (Figure 5.20 and Table 5.12).

Table 5.11: Compressive strength of concrete mixes with RSS and unprocessed fly ash in MPa (Series 3).

Mix	Compressive strength (MPa)				
	1 day	7 days	28 days	90 days	300 days
CMRef	14.8	32.0	42.1	42.7	50.5
CM1	13.3	21.8	23.7	26.5	32.4
CM2	7.4	23.7	30.9	31.0	38.2
CM3	6.3	20.2	31.6	38.3	42.5
CM4	7.2	16.5	31.6	33.2	39.3

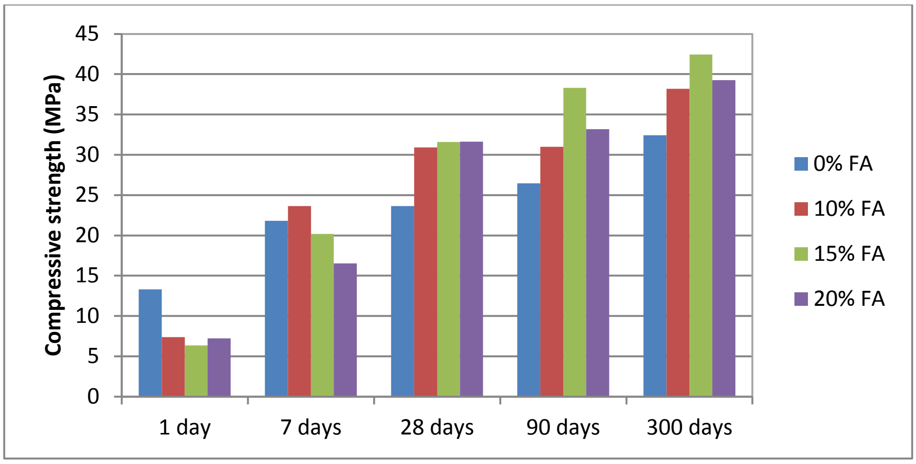


Figure 5.19: Compressive strength of concrete mixes with RSS and unprocessed fly ash (Series 3).

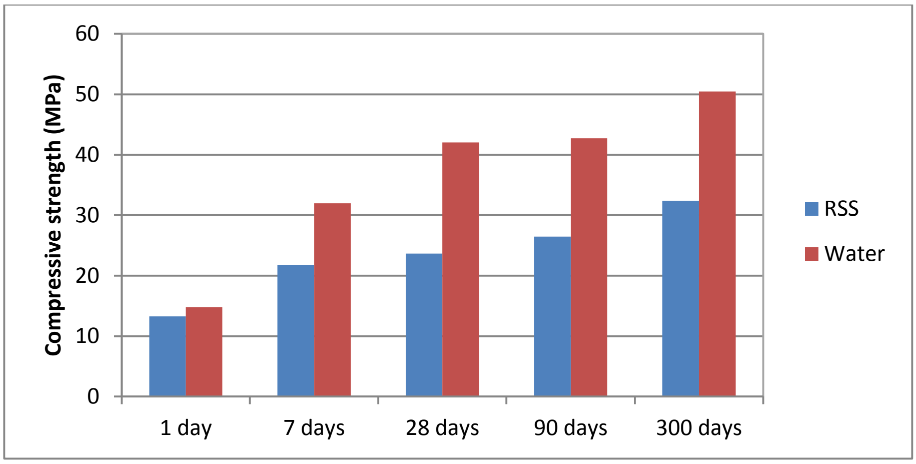


Figure 5.20: Compressive strength of concrete mixes with RSS and water (Series 3).

Table 5.12: Relative compressive strength of concrete mixes with RSS in comparison to those made with water (Series 3).

Mixes	Fly ash %	Relative compressive strength (%)				
		1 day	7 days	28 days	90 days	300 days
CM1/CMRef	0	90	68	56	62	64

5.4.3 Flexural Strength

5.4.3.1 Series 1: Mortar mixes with RSS and unprocessed fly ash

The flexural strength of this series is presented in Table 5.13. The flexural strength results for each group in this series are as follows:

Influence of RSS (Group 1)

Figure 5.21 shows the flexural strength of the mortar mixes with different RSS content. This group of mixes (M1, M2, M3 and M4) incorporated a constant sand to cement ratio of 4.5, 0% unprocessed fly ash and four RSS/Cement ratios of 0.5, 0.65, 0.8 and 1. For comparison purposes, M14 (which contained drinking water equivalent to the water content of M3) was also investigated and considered as the control. Mortar specimens were tested for their flexural strength at 7, 28, 90 and 365 days, and the average strength of three prisms were recorded to the nearest 0.1 MPa. The figure shows a clear trend in flexural strength with RSS content, as strength decreased when the content of RSS increased, except for M3 (RSS/cement ratio=0.8) at 90 and 365 days. The greatest flexural strength was achieved for the mortar mix with RSS/Cement ratio of 0.5 (M1) at all curing ages. Although development of the flexural strength with curing age was not significant, the results showed that the strength developed steadily until 365 days. In addition, no significant differences in flexural strength were observed between the mortar mix with RSS (M3) and the one with water (M14) at both 7 and 365 days. However, some minor differences were observed at 28 and 90 days (Figure 5.25A).

Table 5.13: Flexural strength of mortar mixes with RSS and unprocessed fly ash in MPa (Series 1).

Mix	Flexural strength (MPa)			
	7 days	28 days	90 days	365 days
M1	5.3	5.7	6.3	6.5
M2	4.9	5.4	5.4	5.5
M3	3.9	4.8	5.8	6.1
M4	2.8	4.0	4.8	5.2
M5	Not Determined			
M6				
M7				
M8	2.8	3.7	5.4	5.0
M9	2.4	3.9	5.3	5.3
M10	2.2	3.5	5.3	5.3
M11	4.4	5.1	6.5	6.7
M12	3.5	5.1	6.1	6.9
M13	3.2	4.0	5.3	6.1
M14	4.1	5.5	6.4	6.0
M15	3.1	4.3	5.2	5.1
M16	3.2	4.1	5.1	5.2
M17	4.3	3.6	5.2	5.2

Not Determined: Group 2 was not investigated for this property.

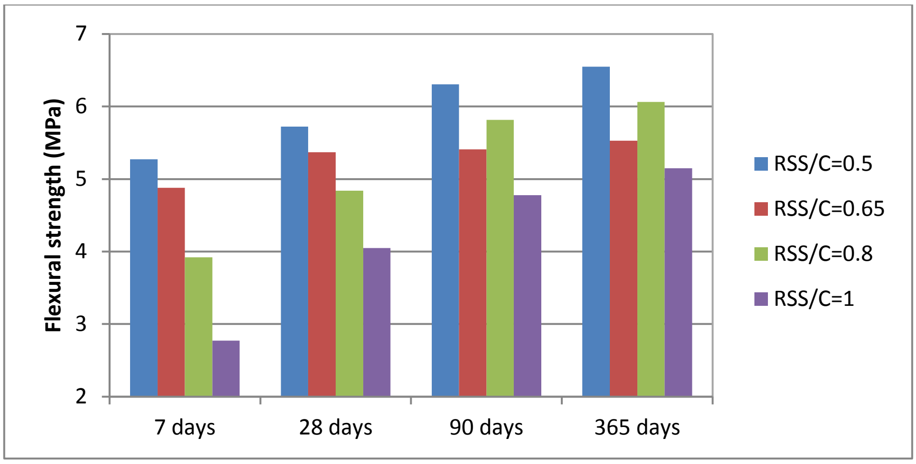


Figure 5.21: Flexural strength of mortar mixes with different RSS content (Group 1).

Influence of fly ash (Groups 3 and 4)

Flexural strength of the mortar mixes with RSS and different proportions of unprocessed fly ash is shown in Figure 5.22 and Figure 5.23. Two groups of mortar mixes that contained a constant sand to cement ratio of 4.5 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder) were examined. Group 3 (M2, M11, M12 and M13) was prepared with a RSS/Binder ratio of 0.65 whilst Group 4 (M3, M8, M9 and M10) was prepared with a RSS/Binder ratio of 0.8. Figure 5.22 shows that the flexural strength at 7 and 28 days decreased when the content of unprocessed fly ash increased and the best strength was recorded for the mortar mix with 0% unprocessed fly ash (M2). At later ages (90 and 365 days), the flexural strength improved with the inclusion of 10 and 20% unprocessed fly ash, and the greatest strength at 90 days was recorded for the mortar mix with 10% fly ash (M11), and at 365 days was recorded for the mortar mix with 20% unprocessed fly ash (M12). For Group 4, (Figure 5.23), the results showed that the flexural strength decreased with the inclusion of unprocessed fly ash, and the greatest results were therefore recorded for the mix with 0% unprocessed fly ash (M3) at all curing ages.

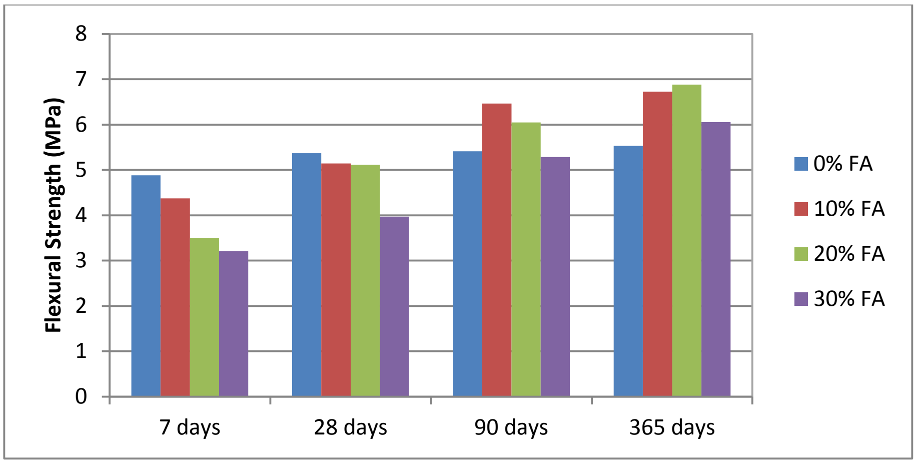


Figure 5.22: Flexural strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3).

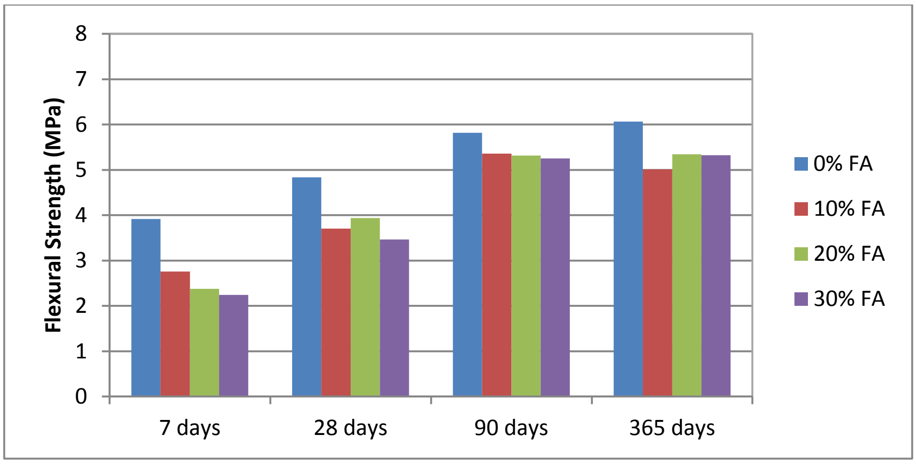


Figure 5.23: Flexural strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4).

Influence of fly ash in the control (Group 5)

Flexural strength of the control mixes is shown in Figure 5.24. This group of mixes (M14, M15, M16 and M17) contained a constant sand to cement ratio of 4.5, Water/Binder ratio of 0.8 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder). The results showed no significant improvement in flexural strength when unprocessed fly ash was included, and the greatest results were therefore recorded for the mix with 0% fly ash (M14).

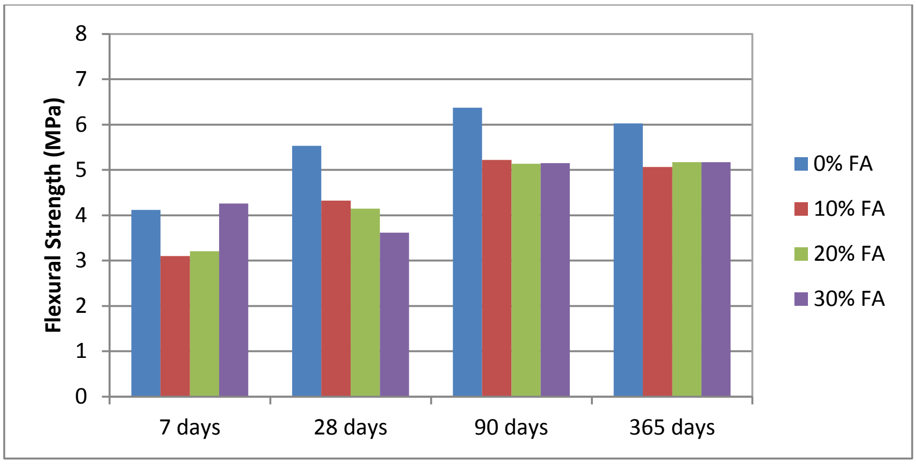
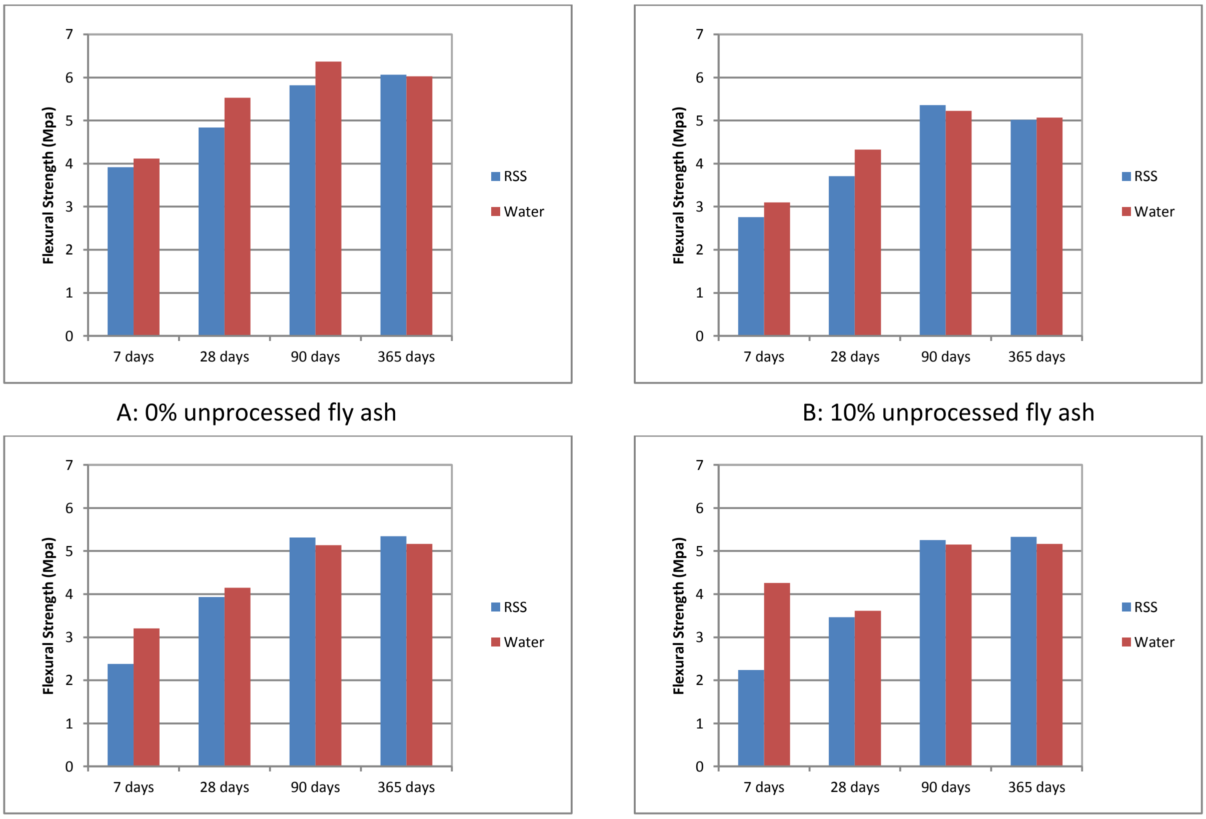


Figure 5.24: Flexural strength of control mixes with different unprocessed fly ash replacements and Water/Binder ratio of 0.8 (Group 5).

The flexural strength of the mortar mixes with water and RSS is shown in Figure 5.25, and the relative flexural strength of the mortar mixes made with RSS in comparison to those made with water is shown in Table 5.14. The relative flexural strength ranged between 53-95% at 7 days, 88-96% at 28 days, 91-104% at 90 days, and 90-103% at 365 days.



A: 0% unprocessed fly ash

B: 10% unprocessed fly ash

C: 20% unprocessed fly ash

D: 30% unprocessed fly ash

Figure 5.25: Flexural strength of mortar mixes with water and RSS.

Table 5.14: Relative flexural strength (%) of the mortar mixes with RSS in comparison to those made with water.

Mixes	Fly ash %	Relative flexural strength (%)			
		7 days	28 days	90 days	365 days
M3/M14	0	95	88	91	101
M8/M15	10	89	86	103	99
M9/M16	20	74	95	104	103
M10/M17	30	53	96	102	103

5.4.3.2 Series 2: Mortar mixes with RSS and large proportions of unprocessed fly ash

The flexural strength property was not determined for this series.

5.4.3.3 Series 3: Concrete mixes with RSS and unprocessed fly ash

Flexural strength of the concrete mixes is shown Table 5.15 and Figure 5.26. This series included four mixes that contained a constant cement:sand:gravel ratio of 1:1.5:3 respectively and Liquid/Binder ratio of 0.5. Cement was replaced with 0, 10, 15 and 20% unprocessed fly ash by weight of total binder. One more concrete mix (CMRef) that contained drinking water (water/Binder ratio of 0.5) was also investigated and considered as the control. Specimens were tested for their flexural strength at 28 days only. The results clearly showed that the flexural strength improved with the inclusion of unprocessed fly ash, and the greatest strength was recorded for the concrete mix with 20% unprocessed fly ash (CM4). The results also showed that the flexural strength of the control mix (CMRef) was relatively greater than that for the mix with RSS. The relative flexural strength (MC1/MCRef) was 79%.

Table 5.15: Flexural strength of concrete mixes incorporating RSS and unprocessed fly ash at 28 days (Series 3).

Mix	Flexural strength (MPa)
CM1	3.8
CM2	4.3
CM3	4.4
CM4	4.9
CMRef	4.8

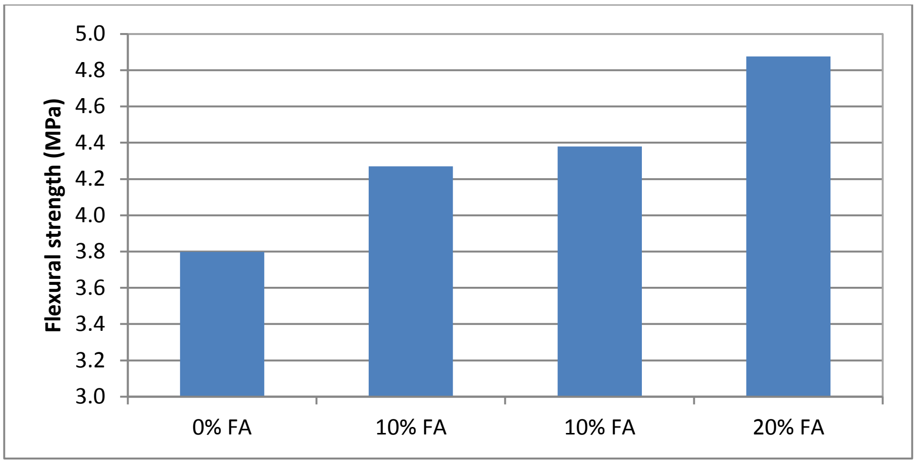


Figure 5.26: Flexural strength of concrete mixes with RSS and unprocessed fly ash at 28 days (Series 3).

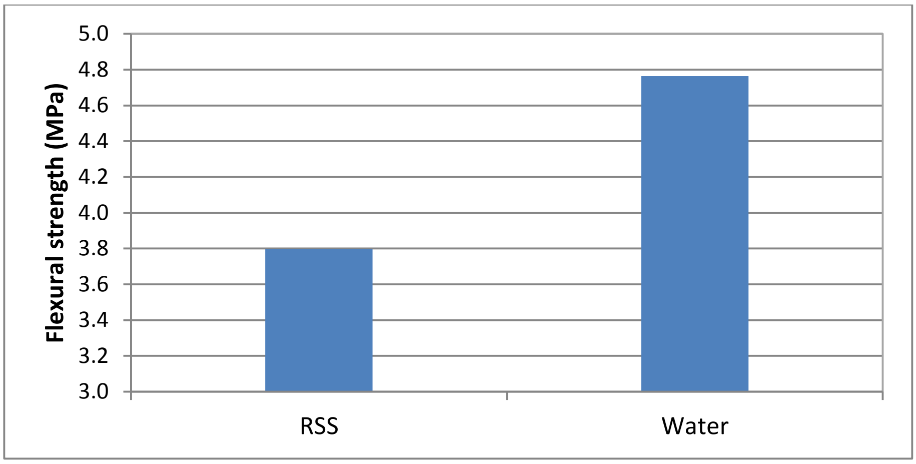


Figure 5.27: Flexural strength of concrete mixes with RSS and water at 28 days (Series 3).

5.4.4 Length Change Due to Drying Shrinkage

5.4.4.1 Series 1: Mortar mixes with RSS and unprocessed fly ash

Influence of RSS (Group 1)

The drying shrinkage of the mortar mixes with different RSS content is shown in Figure 5.28. This group of mixes (M1, M2, M3 and M4) incorporated a constant sand to cement ratio of 4.5, 0% unprocessed fly ash and four RSS/Cement ratios of 0.5, 0.65, 0.8 and 1. For comparison purposes, M14 (which contained drinking water equivalent to the water content of M3), was also included and considered as the control. Drying shrinkage was monitored for mortar specimens between 1 to 365 days. The results showed that drying shrinkage generally increased when the content of RSS increased. The results also showed that most of the drying shrinkage occurred during the first 50- 70 days. Moreover, no significant difference in drying shrinkage was observed between the control mix (M14) and its corresponding mix with RSS (Figure 5.29).

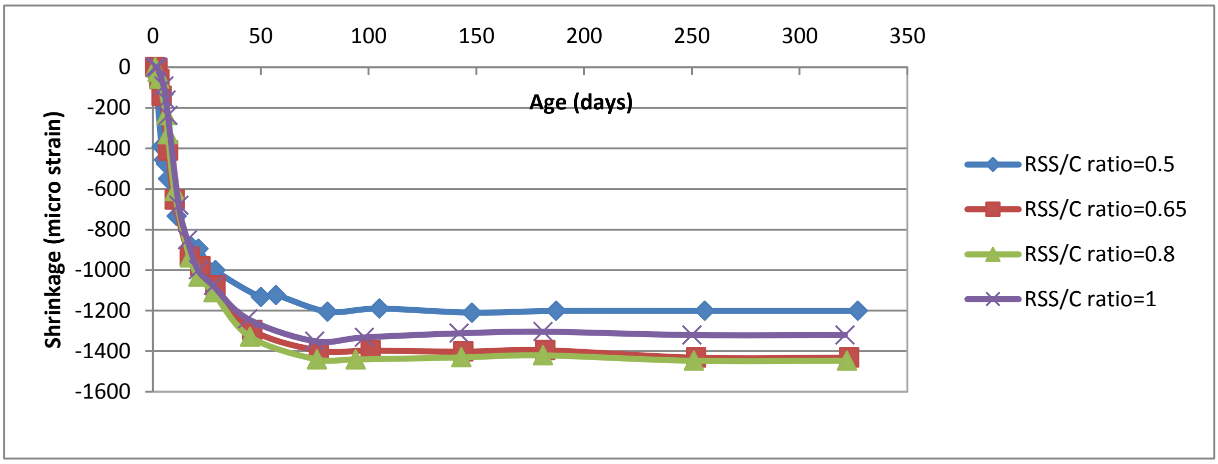


Figure 5.28: Drying shrinkage of the mortar mixes with different RSS content (Group 1).

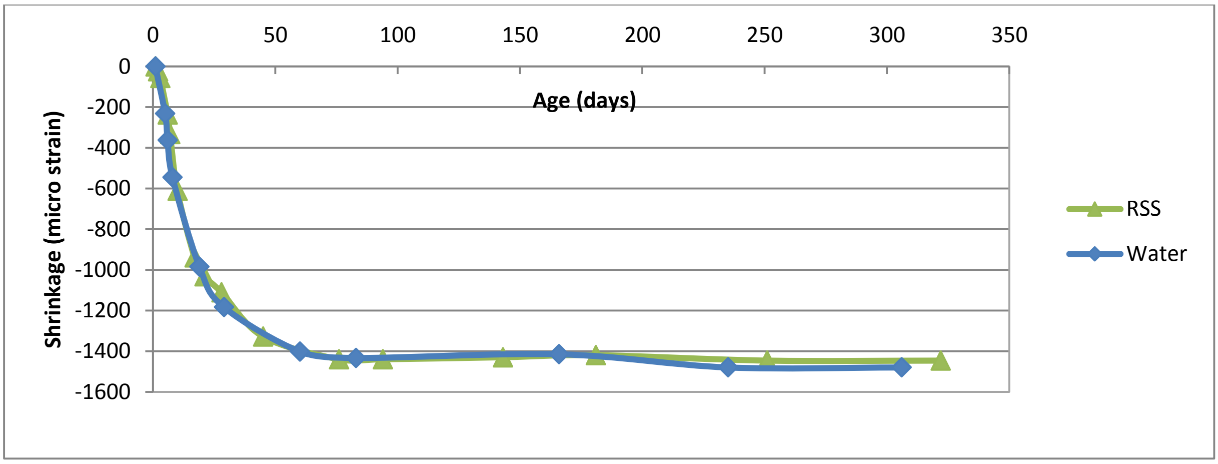


Figure 5.29: Drying shrinkage of mortar mixes with RSS and water.

Influence of fly ash (Groups 3 and 4)

Drying shrinkage for the mortar mixes with RSS and different proportions of unprocessed fly ash is shown in Figure 5.30 and Figure 5.31. The results clearly showed that drying shrinkage decreased when unprocessed fly ash content increased for both Groups 3 and 4 (RSS/Binder ratios 0.65 and 0.8 respectively). The results also showed that drying shrinkage of Group 3 (RSS/Binder ratio of 0.65) was comparatively less than that for Group 4 (RSS/Binder ratio of 0.8). Moreover, both figures show that drying shrinkage mostly occurred during the first 50-70 days, through which no significant differences in drying shrinkage with unprocessed fly ash content were observed.

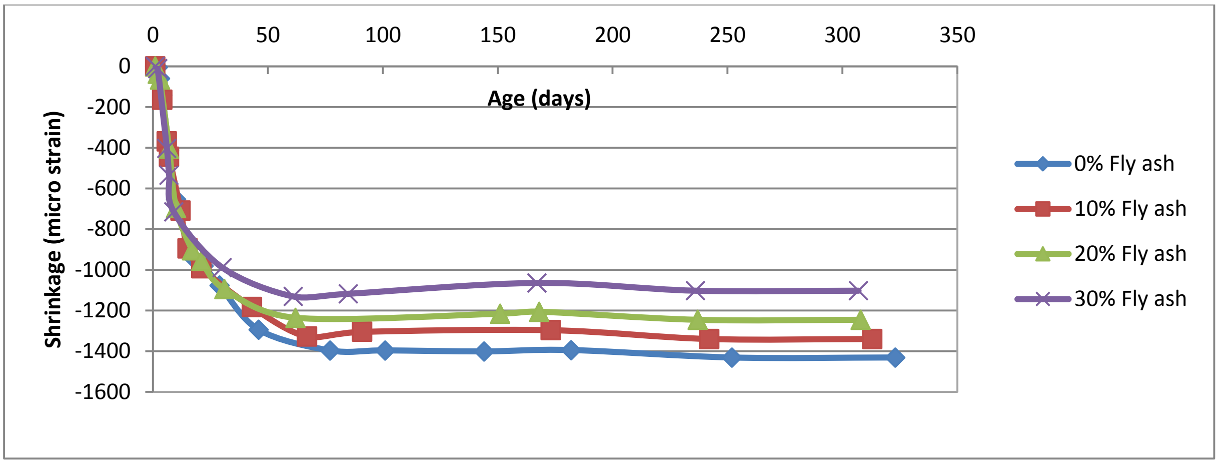


Figure 5.30: Drying shrinkage of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3).

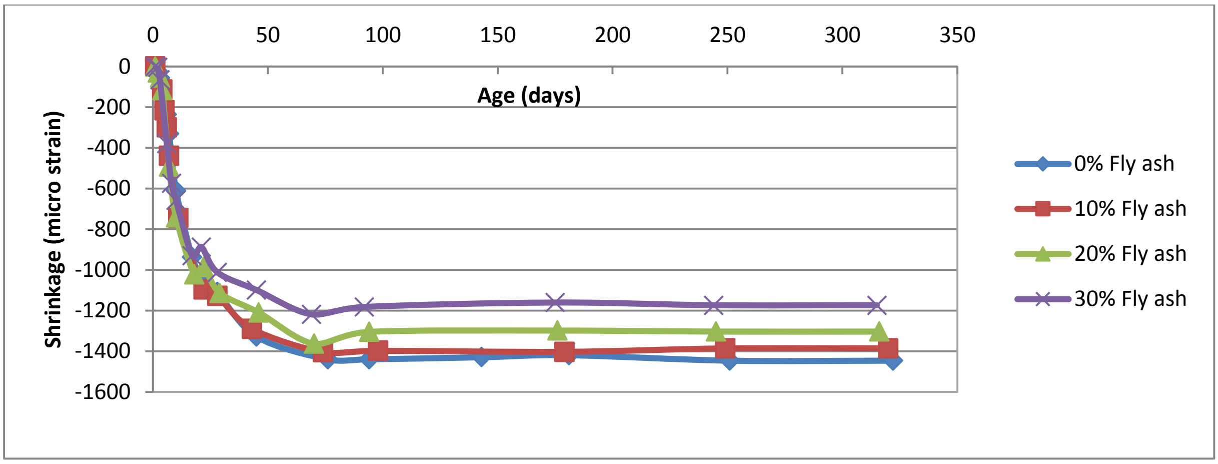


Figure 5.31: Drying shrinkage of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4).

Influence of fly ash in the control (Group 5)

Drying shrinkage of the control mixes is shown in Figure 5.32. This group of mixes (M14, M15, M16 and M17) contained a constant sand to cement ratio 4.5, Water/Binder ratio of 0.8 and four proportions of unprocessed fly ash (0, 10, 20 and 30% by weight of total binder). The figure shows that drying shrinkage mostly occurred during the first 50 days, on which no significant differences with unprocessed fly ash content were observed. At later ages, the results generally showed that drying shrinkage decreased when unprocessed fly ash content was increased except for the mortar mix with 20% unprocessed fly ash (M16).

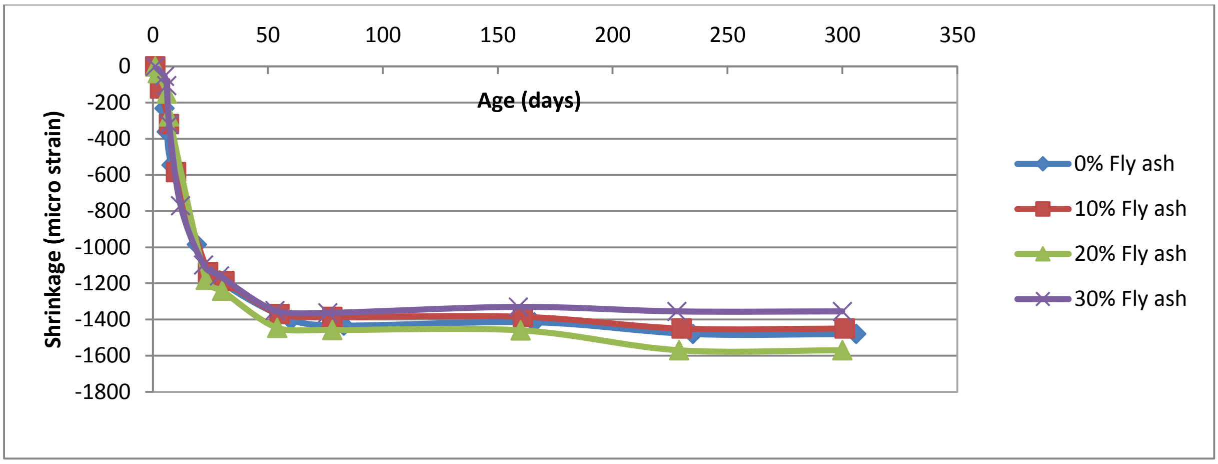


Figure 5.32: Drying shrinkage of the control mixes with different unprocessed fly ash content and Water/Binder ratio of 0.8 (Group 5).

5.4.4.2 Series 2: Mortar mixes with RSS and large proportions of unprocessed fly ash

Drying shrinkage was not determined for this Series.

5.4.4.3 Series 3: Concrete mixes with RSS and unprocessed fly ash

Drying shrinkage of the concrete mixes is shown in Figure 5.33. This series included four mixes that incorporated constant cement:sand:gravel ratio of 1:1.5:3 respectively and Liquid/Binder ratio of 0.5. Cement was replaced with 0, 10, 15, and 20% unprocessed fly ash by weight of total binder. One more concrete mix (CMRef), made of drinking water with Water/Binder ratio of 0.5, was investigated and considered as the control. The figure clearly demonstrates that drying shrinkage decreased when the content of unprocessed fly ash increased for all mixes in this series. The results also showed that drying shrinkage increased when water was replaced with RSS (Figure 5.34).

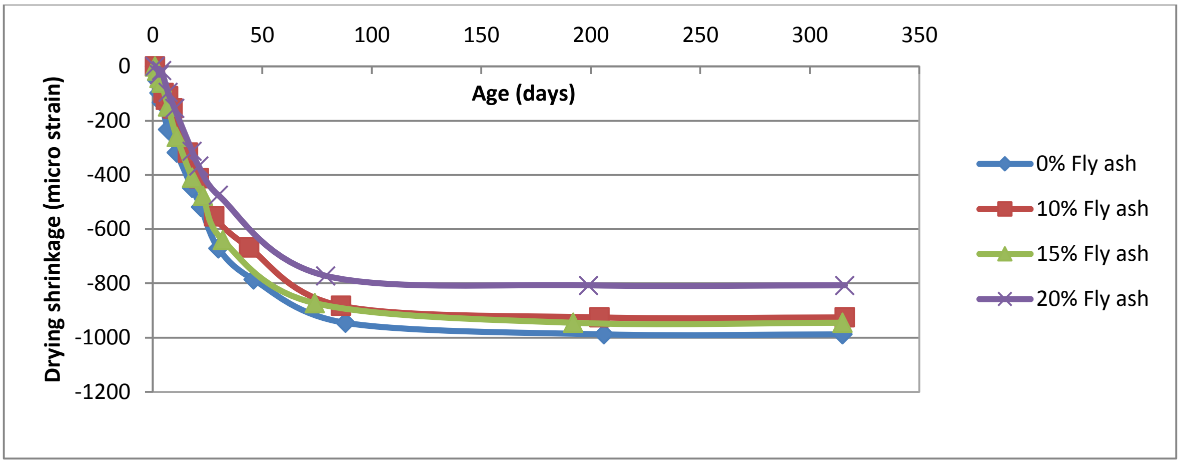


Figure 5.33: Drying shrinkage of concrete mixes with RSS and unprocessed fly ash (Series 3).

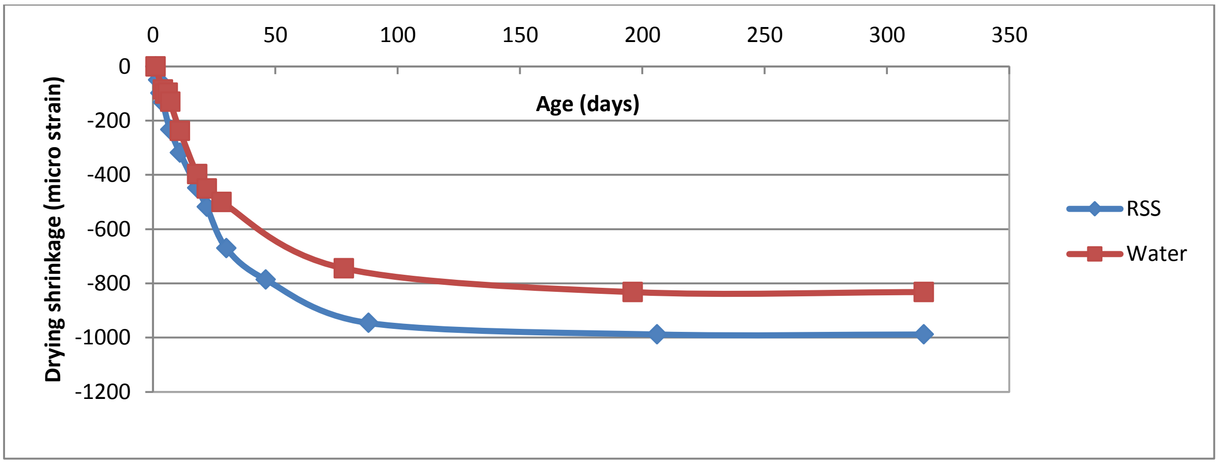


Figure 5.34: Drying shrinkage of concrete mixes with RSS and water (Series 3).

5.5 CONCLUSIONS

This chapter examined the mechanical properties of cement-based systems that contained RSS and unprocessed fly ash. Three series of cement-based materials were examined for their UPV, compressive strength, flexural strength and drying shrinkage. Cement-based materials included mortar mixes with RSS and unprocessed fly ash (Series 1), mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2), and concrete mixes with RSS and unprocessed fly ash (Series 3). The main conclusions of this chapter are summarised below:

- <u>**Ultrasonic Pulse Velocity (UPV)**</u>
    - Group 1: UPV values increased when RSS content reduced at curing ages and the greatest UPV values were recorded for the mortar mix with RSS/Cement ratio of 0.5, which ranged between 3429-4144 m/s. UPV values of the mortar mix with

RSS (M3) were comparatively less than those for the mix with water (M14). The relative UPV ranged between 87.2-97%. UPV values improved with the curing age. However the greatest UPV values were not necessary achieved at 365 days, but at earlier ages (28 or 90 days).

- Group 2: The results generally showed that UPV values increased when the sand to cement ratio also increased up to 6, and the greatest UPV values were achieved at either 28 or 90 days.
- Groups 3 and 4: UPV values generally decreased with the inclusion of unprocessed fly ash at all curing ages. UPV values for the mixes with RSS/Binder ratio of 0.65 (Group 3) were comparatively greater than those with RSS/Binder ratio of 0.8 (Group 4). The UPV values for Group 3 ranged between 2799-3896 m/s, and for Group 4 ranged between 2562-3555 m/s.
- Group 5: For the control mixes, UPV values at 1, 7 and 28 days decreased when the unprocessed fly ash content increased and the greatest UPV readings were recorded for the mortar mix with 0% unprocessed fly ash (M14). At 90 and 365 days, UPV increased with the inclusion of unprocessed fly ash. UPV values of the mortar mixes with RSS were comparatively less than those for the mixes with water and the relative UPV values ranged between 87.2-109.7% at 1 day, 96.8-100.9% at 7 days, 95.3-100.5% at 28 days, 93.2-95.5% at 90 days, and 88.4-91.8% at 365 days.
- Series 2: For the mortar mixes with large proportion of unprocessed fly ash, UPV generally decreased when the content of unprocessed fly ash increased. The results also showed that UPV values of the control mix were comparatively greater than those for the mix with RSS and the relative UPV values ranged between 84.4-100.5%.
- Series 3: For the concrete mixes, the results showed that the addition of unprocessed fly ash did not significantly influence UPV at all curing ages except at 1 day (UPV decreased when unprocessed fly ash was added up to 15% of total binder weight). The values of the control mix were comparatively greater than those for the mix with RSS and the relative UPV ranged between 93.7-97.3%.

- **Compressive Strength**
    - Group 1: The compressive strength decreased when the content of RSS increased and the greatest compressive strength was achieved for the mortar mix with RSS/Cement ratio of 0.5 (between 10.7-43.7 MPa). Moreover, compressive strength of the mortar mix with RSS (M3) was fairly good in comparison with the

mix that contained drinking water (M14), and the relative strength ranged between 56-70%.

- Group 2: The compressive strength generally reduced when the sand content increased and the greater compressive strength was achieve for the mortar mix with sand to cement ratio of 3 (between 2.3-22.2 MPa).
- Groups 3 and 4: For the mortar mixes with unprocessed fly ash and RSS/Binder ratio of 0.65 (Group 3), it was observed that the compressive strength at 1, 7 and 28 days generally decreased when the content of unprocessed fly ash increased. At later ages (90 and 365 days), the results showed certain improvement in compressive strength when cement was replaced by unprocessed fly ash at 20%. The greatest compressive strength was 29.2 MPa.
- Group 4: For the mortar mixes that contained unprocessed fly ash and a RSS/Binder ratio of 0.8 (Group 4), the results showed that the compressive strength increased when the content of unprocessed fly ash also increased, and the greatest compressive strength values of 19.9 and 19.8 MPa were achieved for the mortar mixes with 10 and 20% unprocessed fly ash (M8 and M9 respectively). The addition of unprocessed fly ash improved long-term strength development, and prevented the fall in compressive strength observed in all mixes with RSS only at 365 days.
- Group 5: For the control mixes, the compressive strength at 1, 7, 28 and 90 days decreased when unprocessed fly ash content increased. At later ages (365 days) the results showed a noticeable improvement in compressive strength for all mixes that contained unprocessed fly ash, and the greatest compressive strength of 26.4 MPa was recorded for the mix with 10% unprocessed fly ash (M15). The compressive strength of the specimens that contained RSS was noticeably less than that of the mixes with water, and the relative compressive strength ranged between 56-97% at 1 day, 62-94% at 7 days, 60-105% at 28 days, 74-99% at 90 days, and 70-78% at 365 days.
- Series 2: For the mortar mixes with RSS and large proportions of unprocessed fly ash, the compressive strength decreased with the inclusion of unprocessed fly ash. The results also demonstrated that the compressive strength of the control mix was comparatively greater than that contained RSS. The relative compressive strength values of ML1/MLRef ranged between 86.3-95.2%.
- Series 3: For the concrete mixes, the results showed that the compressive strength at 1 and 7 days generally decreased when the content of unprocessed fly ash increased. At 28 days, the compressive strength improved when the cement was replaced with unprocessed fly ash at 10-20%. The results also

showed that replacing cement with 15% unprocessed fly ash significantly improved long-term compressive strength (at 90 and 300 days). Moreover, compressive strength of concrete mix with RSS was fairly good in comparison with the mix that contained drinking water. The relative compressive strength values of CM1/CMRef ranged between 56-90%.

- **<u>Flexural Strength</u>**
    - Group 1: For mortar mixes with different RSS content, the flexural strength generally decreased when the content of RSS increased.
    - Groups 3 and 4: For mortar mixes with unprocessed fly ash and RSS/Binder ratio of 0.65 (Group 3), the flexural strength at 7 and 28 days decreased when the content of unprocessed fly ash was increased. At later ages (90 and 365 days), the flexural strength was improved when cement was replaced with unprocessed fly ash by 10 and 20%. For the mortar mixes with unprocessed fly ash and a RSS/Binder ratio of 0.8 (Group 4), the results showed no significant improvement in flexural strength when unprocessed fly ash was included.
    - Group 5: For the control mixes, no significant improvement in flexural strength was observed when unprocessed fly ash was included. Additionally, no significant differences in flexural strength were observed between the mortar mixes that container RSS (Group 4) and those made with water (Group 5). The relative flexural strength ranged between 53-95% at 7 days, 88-96% at 28 days, 91-104% at 90 days, and 90-103% at 365 days.
    - Series 3: For the concrete mixes, the results clearly showed that the flexural strength was improved when unprocessed fly ash content was increased and the greatest strength was recorded for the mix with 20% unprocessed fly ash (CM4). The results also showed that the flexural strength of the control mix (CMRef) was relatively greater than that for the mix with RSS. The relative flexural strength (MC1/MCRef) was 79%.

- **<u>Drying Shrinkage</u>**
    - Group 1: The drying shrinkage generally increased when the content of RSS also increased. No significant difference in drying shrinkage was observed between the control mix (M14) and its corresponding mix with RSS (M3).
    - Groups 3 and 4: For the mortar mixes with unprocessed fly ash and RSS, the results clearly showed that drying shrinkage decreased with the inclusion of unprocessed fly ash for both RSS/Binder ratios.

- Group 5: For the control mixes, the drying shrinkage mostly occurred in the first 50 days, during which no significant differences were observed when unprocessed fly ash was added. At later ages, the results generally showed that drying shrinkage decreased when unprocessed fly ash content increased.
- Series 3: For the concrete mixes, the results demonstrated that drying shrinkage decreased when the content of unprocessed fly ash was increased for all mixes in this series. The results also showed that drying shrinkage increased when water was replaced with RSS.

CHAPTER 6: SULPHATE RESISTANCE

6.1 INTRODUCTION

The hydration process of cement-based materials produces portlandite $Ca(OH)_2$, which when leaching increases the ingress of sulphate ions into hardened concrete. The reaction of the hydration products with sulphate is likely to produce more gypsum ($CaSO_4$) and more ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$), which are responsible for more expansion (Rozière et al., 2009). There are typically two types of sulphate attack: the first one is resulting from the reaction of alumina-bearing hydration products, and/or unhydrated tricalcium aluminate (C_3A) with sulphate and thus ettringite is produced; the second type is resulting from the reaction of sulphate with calcium hydroxide to produce gypsum. Gypsum can be produced during sulphate attack through cation exchange reactions. The formation of ettringite in hardened concrete, due to sulphate attack, generates internal expansive strain result in expansion. Thus the formation of ettringite can lead to cracking and reduced performance, subject to the concrete quality. Sulphate attack through gypsum formation can result in smaller expansion than the ettringite attack, but is more generally known to manifest itself through loss of stiffness and strength (Tian and Cohen, 2000; Santhanam et al., 2002; Monteiroa and Kurtisb, 2003).

In addition to the formation of both ettringite and gypsum and its subsequent expansion, the deterioration of cement-based materials due to sulphate attack is partially caused by the degradation of calcium silicate hydrate (C–S–H) gel through leaching of the calcium compounds. This process leads to loss in stiffness of C–S–H gel and overall deterioration of the cement-based materials (Mehta, 1983). Expansion and cracking are generally attributed to the expansive forces generated by ettringite formation due to the reaction of sulphate with the calcium aluminium hydrates. The loss of weight and strength are generally attributed to reactions where sulphate attacks and breaks down the calcium silicate hydrate (C–S–H), which is the main binding component of hardened cement (Higgins, 2003).

The resistance of cement-based materials to sulphate attack can be improved by providing physical barriers including water proofing. Alternatives include using sulphate-resisting cement (Type V), which contains less than 3.5% of C_3A (BSI, 1996b). Sulphate resistance can also be improved by including other pozzolanic additives such as fly ash. The incorporation of fly ash products into the cement-based system is well known to positively contribute to sulphate resistance (Dikeou, 1970; Harmann and Mangotich, 1987; Tikalsky and Carrasquillo, 1989; Dhole et al., 2009).

6.2 AIMS AND OBJECTIVES

The aim of this chapter is to evaluate the resistance of cement-based materials that incorporated RSS and unprocessed fly ash to sulphate attack. Two series of cement-based materials, including mortar and concrete mixes, were therefore assessed. Sulphate attack was evaluated by measuring changes in weight, compressive strength and visual observation during approximately 365 days of continuous exposure to sulphate solution.

6.3 MATERIALS, MIXING PROPORTIONS, PREPARATIONS AND TESTING

Several construction materials were used to prepare mortar and concrete specimens for sulphate attack test. These include Portland cement, fine aggregate, coarse aggregate, drinking water, Raw Sewage Sludge (RSS) and unprocessed fly ash. More details about materials properties are available in Section 3.3.

Two series of cement-based mixes were evaluated for their resistance to sulphate attack. This included mortar mixes with RSS and unprocessed fly ash (Series 1), and concrete mixes with RSS and unprocessed fly ash (Series 3). All groups in Series 1 apart from Group 2 were investigated. More details about the mixing proportions can be found in Section 3.3.10.

Steel moulds (50mm in size) were used to cast mortar samples, and 100mm in size steel moulds were used for concrete samples. Cast specimens were covered with plastic sheets and placed in a room at a temperature of 20$\pm$2 ^{o}C for 24 hours until demoulding. Thereafter, samples were wrapped by either a cling film (for mortar sampler) or plastic sheets (for concrete samples) until testing.

Mortar and concrete specimens were cured for 28 days and were immersed in a sulphate solution that was prepared in accordance to PD CEN/TR 15697:2008 (BSI, 2008c). The sulphate solution was prepared by mixing 5% (by weight) sodium sulphate (Na_2SO_4) with 95% (by weight) drinking water. Sulphate attack was evaluated by measuring changes in weight, compressive strength and visual observation during approximately 365 days of continuous exposure to sulphate solution. 18 mortar specimens (50x50x50mm in size) were used for each mix, 15 of which were placed in the sulphate solution immediately after the end of the curing. The remaining 3 were tested without being subjected to sulphate attack and were considered as the reference. Immersed specimens were tested for their compressive strength, weight change and visual inspection (3 at a time) at various time intervals, subject to the deterioration levels. For concrete mixes, 12 concrete specimens (100x100x100mm in size) were used for each mix, 10 of which were immersed in sulphate solution immediately after the end of the curing. The remaining 2 were tested without being subjected to sulphate attack and were considered as the reference. Immersed specimens were tested for their compressive strength, weight change and visual inspection (2 at a time) at various time intervals, subject to the deterioration level. For the mortar mixes, the average compressive strength of three cubes (50 mm in size) was recorded to the nearest 0.1 N/mm^2. For the concrete samples, the average compressive strength of two cubes (100 mm in size) was recorded to the nearest 0.1 N/mm^2. PH level was not monitored and sulphate solution was not changed throughout the course of the test.

6.4 RESULTS

6.4.1 Series 1: Mortar mixes with RSS and unprocessed fly ash

6.4.1.1 Influence of RSS (Group 1)

<u>**Compressive strength**</u>

The compressive strength and relative strength of mortar mixes with different RSS content in sulphate solution is shown in Figure 6.1 and Figure 6.2. Both figures clearly demonstrate that the compressive strength reduced when the content of RSS increased, as well as the strength continued to develop even when the samples were placed in a sulphate solution prior to its subsequent declining at later ages. The best sulphate attack resistance and strength development were seen for the mortar mix with RSS/Cement ratio of 0.5 (M1). Additionally, the compressive strength and the relative compressive strength of the control mix were comparatively higher than that made with RSS, as presented in Figure 6.3 and Figure 6.4.

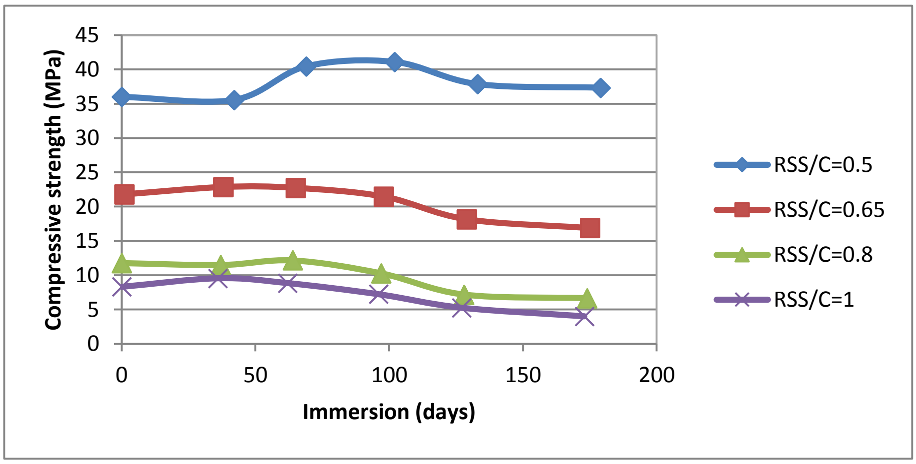


Figure 6.1 : Compressive strength of mortar mixes with different RSS content in sulphate solution (Group 1).

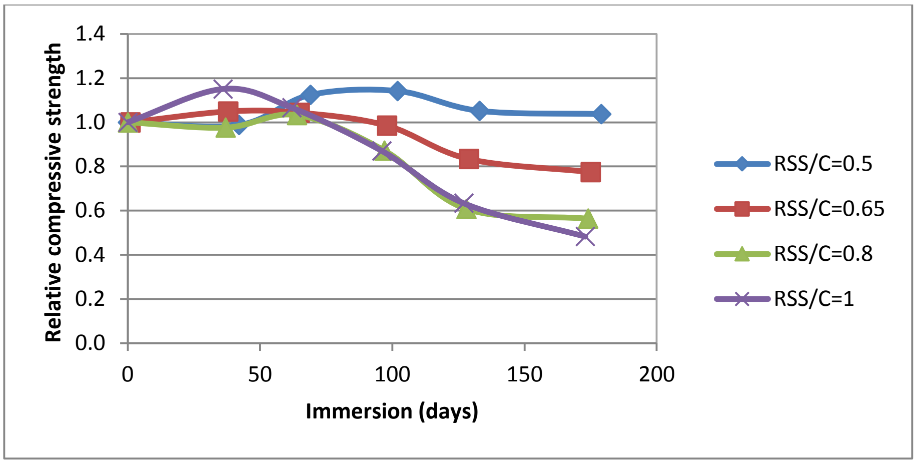


Figure 6.2 : Relative compressive strength of mortar mixes with different RSS content in sulphate solution (Group 1).

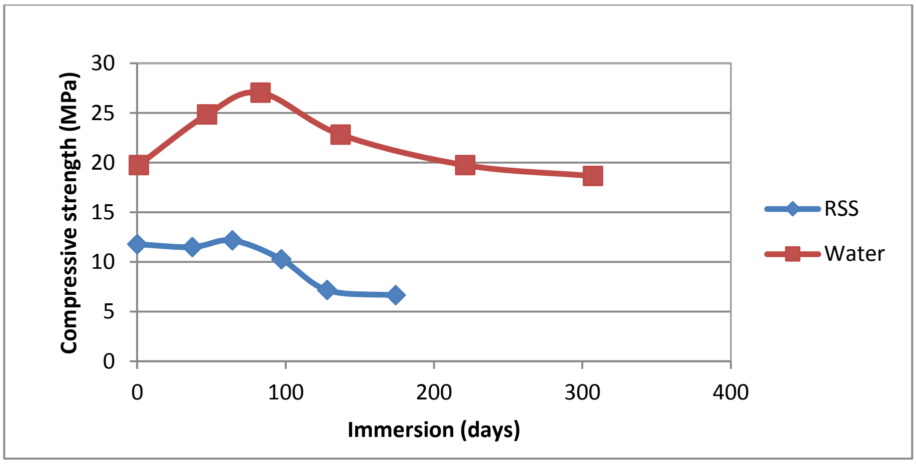


Figure 6.3 : Compressive strength of mortar mixes with RSS and water in sulphate solution.

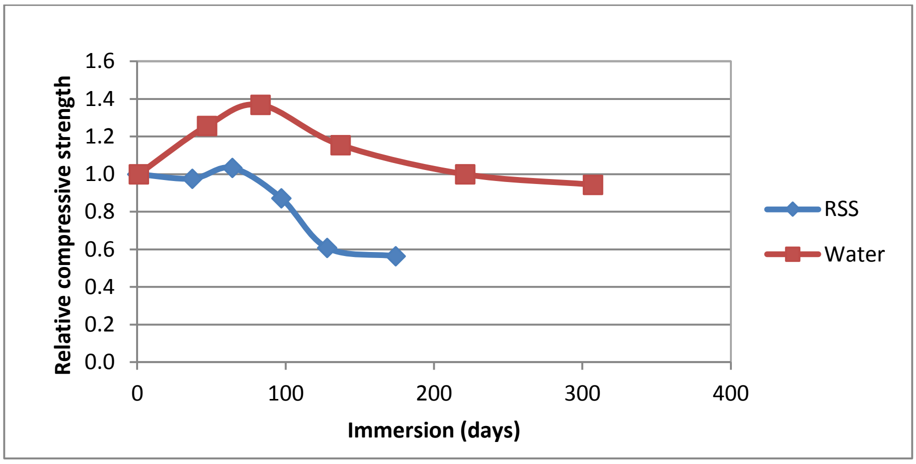


Figure 6.4 : Relative compressive strength of mortar mixes with RSS and water in sulphate solution.

Relative weight

The relative weight of mortar mixes with different RSS content in sulphate solution is presented in Figure 6.5. The relative weight was recorded for the last three specimens in the sulphate solution for each mix. The relative weight was determined by dividing the weight of immersed samples by its original weight and then timed by 100%. For the mortar mixes with RSS/Cement ratio of 1, the relative weight continued to increase until 62 days prior to its subsequent falling. For the mortar mix with RSS/Cement ratio of 0.8, the relative weight increased until 97 days and then started to fall. The reduction in weight was due to loss in mass as a result of the sever deterioration. For the remaining two mixes, the relative weight continued to develop until later ages (175-179). The relative weight of the mortar mixes with RSS and water is shown in Figure 6.6.

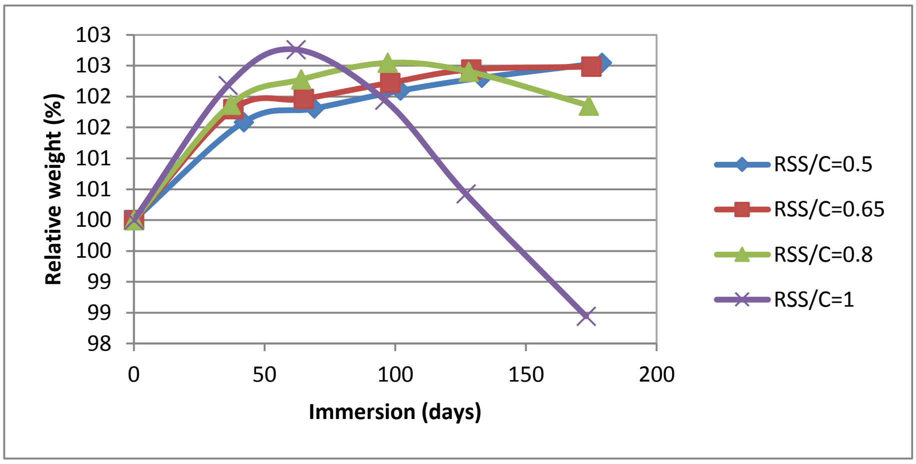


Figure 6.5: Relative weight of mortar mixes with different RSS content in sulphate solution (Group 1).

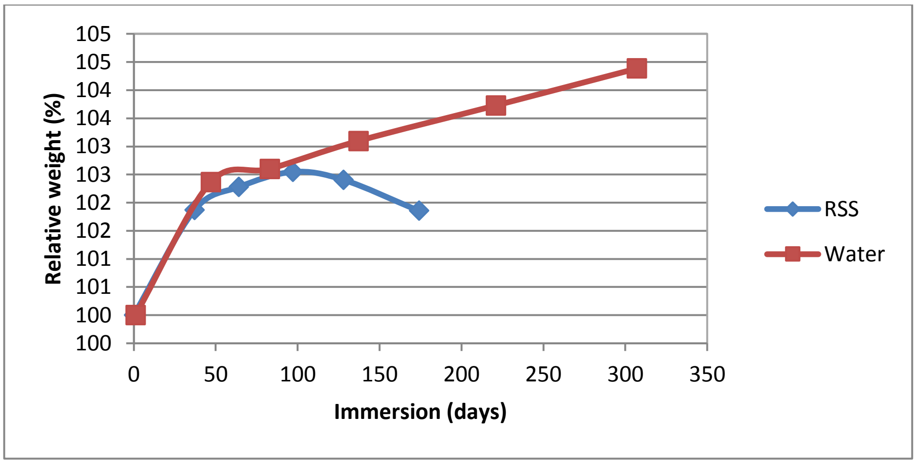


Figure 6.6: Relative weight of mortar mixes with RSS and water in sulphate solution.

Visual observation

The deterioration of mortar mixes with different RSS content in sulphate solution is shown in Figure 6.7. No significant changes were observed during the first month for all mixes; however samples with higher RSS content (RSS/C ratio of 0.8 and 1) started to show initial deterioration after almost 60 days. Deterioration continued severely at later ages for these two mixes. For the mortar mix with RSS/C of 0.65 (M2), the first sign of deterioration was observed at 98 days and it continued to develop badly until 129 days. No signs of deterioration were recorded for the mortar mix with RSS/C of 0.5 until later ages. Additionally, the control mix showed comparatively better resistance to sulphate attack than that made with RSS, as presented in Figure 6.8.

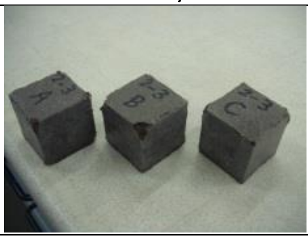
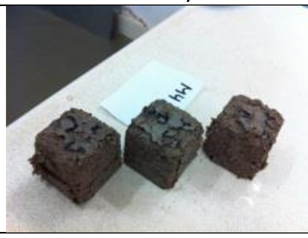
RSS/Cement=0.5	RSS/Cement=0.65	RSS/Cement=0.8	RSS/Cement=1
			
42 days	38 days	37 days	36 days
			
69 days	65 days	64 days	62 days
			
102 days	98 days	97 days	96 days
			
133 days	129 days	128 days	127 days
			
179 days	175 days	174 days	173 days

Figure 6.7 : Deterioration of mortar specimens with different RSS content in sulphate solution (Group 1).

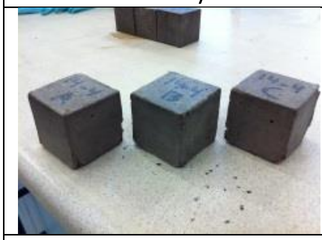
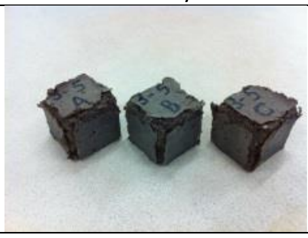
Water	RSS
	
47 days	37 days
	
83 days	64 days
	
137 days	97 days
	
221 days	128 days
	
307 days	174 days

Figure 6.8 : Deterioration of mortar specimens with RSS and water in sulphate solution.

6.4.1.2 Influence of fly ash (Groups 3 and 4)

Compressive strength

The Compressive strength and relative strength of the mortar mixes with different unprocessed fly ash and RSS/Binder ratio of 0.65 (Group 3) is presented in Figure 6.9 and Figure 6.10. For the mortar mixes with RSS/Binder ratio of 0.8 (Group 4), the compressive strength and the relative strength is shown in Figure 6.11 and Figure 6.12. The results firmly demonstrated that the incorporation of unprocessed fly ash significantly improved the sulphate attack resistance, and the best results were observed for the mortar mixes with 30% unprocessed fly ash replacement for both RSS/Binder ratios. For the mixes with 30% unprocessed fly ash, the strength continued to develop with immersion time until the greatest strength was achieved at later ages (320-330 days). For the mortar mixes with less unprocessed fly ash content (10-20% replacement) and RSS/Binder ratio of 0.65, the compressive strength at earlier ages was relatively less than that for the mix with 0% unprocessed fly ash. The compressive strength continued to develop until its subsequent falling at later ages (215 days for the mix with 20% unprocessed fly ash, and 150 days for the mix with 10% unprocessed fly ash). For the mortar mixes with RSS/Binder ratio of 0.8, the results generally showed the same trend. The results also showed that the strength at early ages was greater than that for the mix with 0% unprocessed fly ash. The mortar mix with 20% unprocessed fly ash showed the best compressive strength until 320-330 days when the mix with 30% unprocessed fly ash (M10) took over. Strength development continued to improve for mixes with 30% unprocessed fly ash for both RSS contents, as presented Figure 6.10 and Figure 6.12.

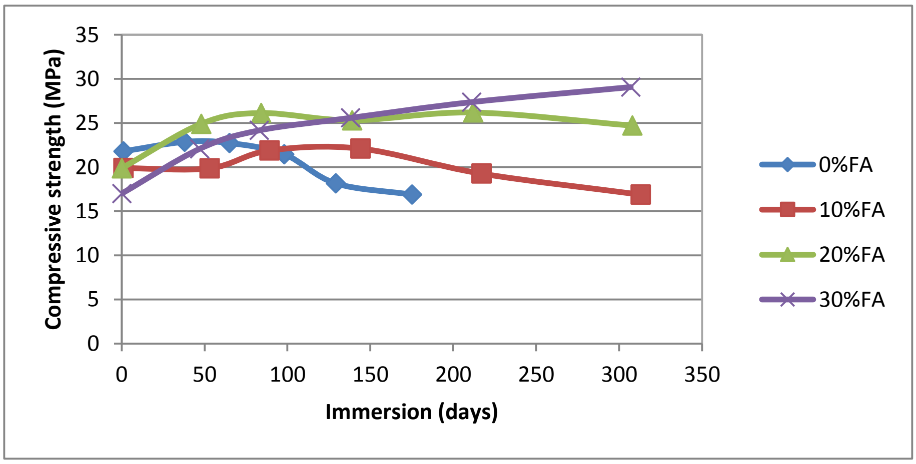


Figure 6.9: Compressive strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio=0.65 in sulphate solution (Group 3).

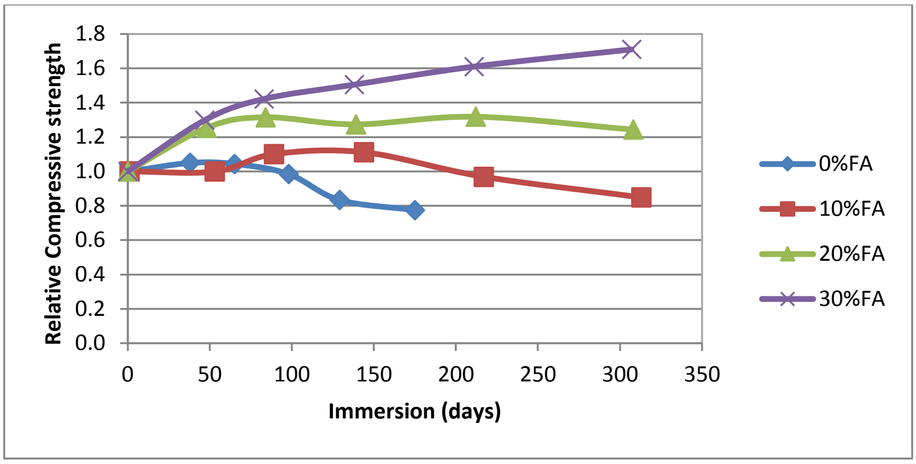


Figure 6.10: Relative strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio=0.65 in sulphate solution (Group 3).

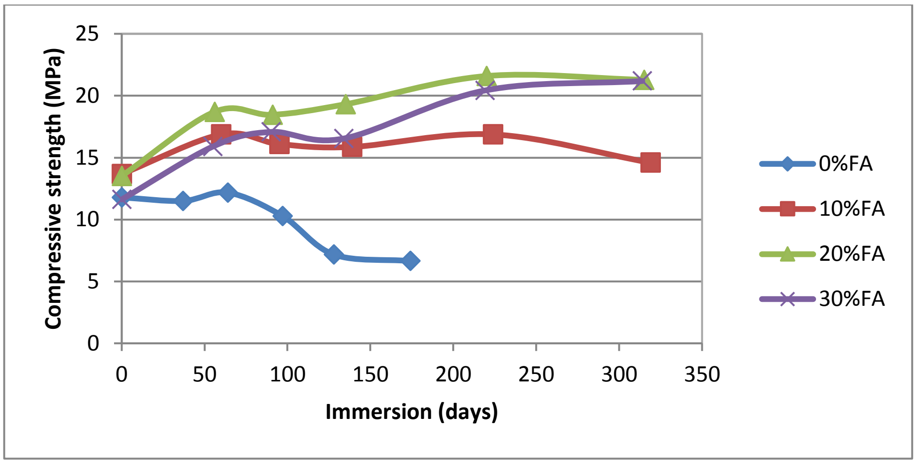


Figure 6.11 : Compressive strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio=0.8 in sulphate solution (Group 4).

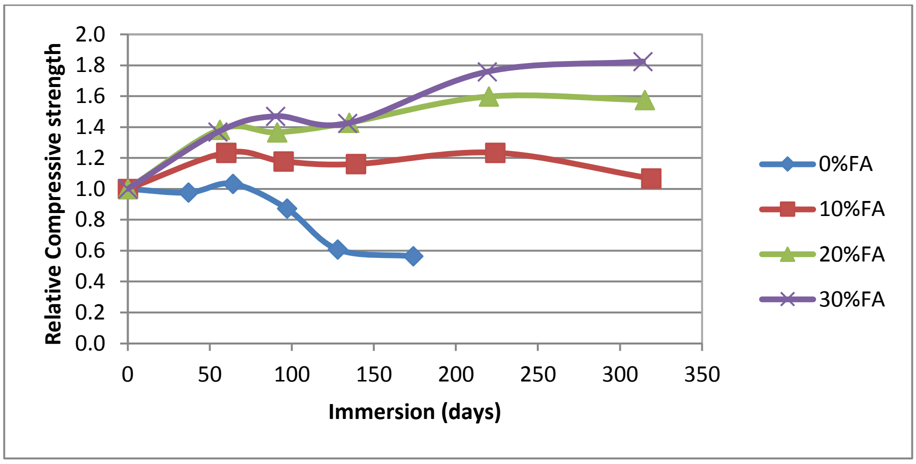


Figure 6.12 : Relative strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio=0.8 in sulphate solution (Group 4).

Relative weight

The relative weight of the mortar mixes with different unprocessed fly ash content (Groups 3 and 4) in sulphate solution is presented in Figure 6.13 and Figure 6.14. The relative weight was recorded for the last three specimens in the sulphate solution for each mix. The relative weight was determined by dividing the weight of immersed samples by its original weight and then timed by 100%. Figure 6.13 shows that the relative weight of the mortar mixes with unprocessed fly ash and RSS/Binder ratio of 0.65 continued to increase during the first 90 days. Thereafter, the weight change was not significant. For the mortar mixes with RSS/Binder ratio of 0.8, the relative weight continued to develop during the first 1 to 90 days. Thereafter, the weight of the mortar mixes with 20-30% unprocessed fly ash replacement remained the same, whereas the weight of the mortar mix with 10% unprocessed fly ash continued to increase.

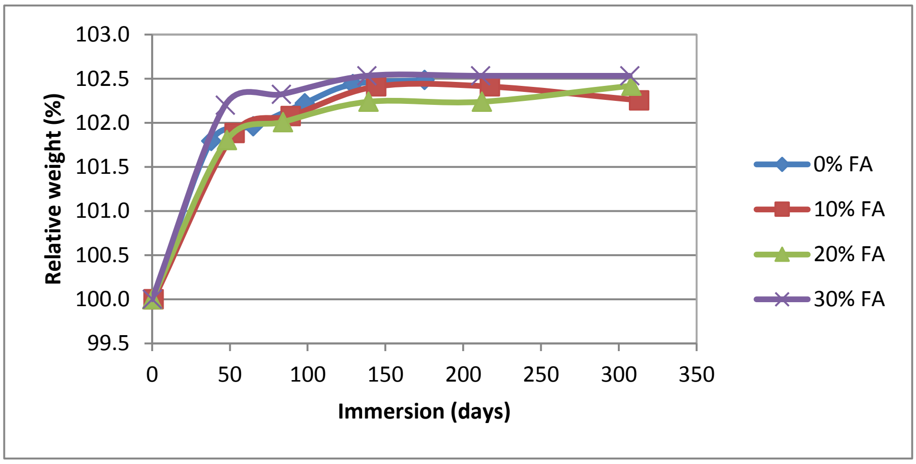


Figure 6.13: Relative weight of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio=0.65 in sulphate solution (Group 3).

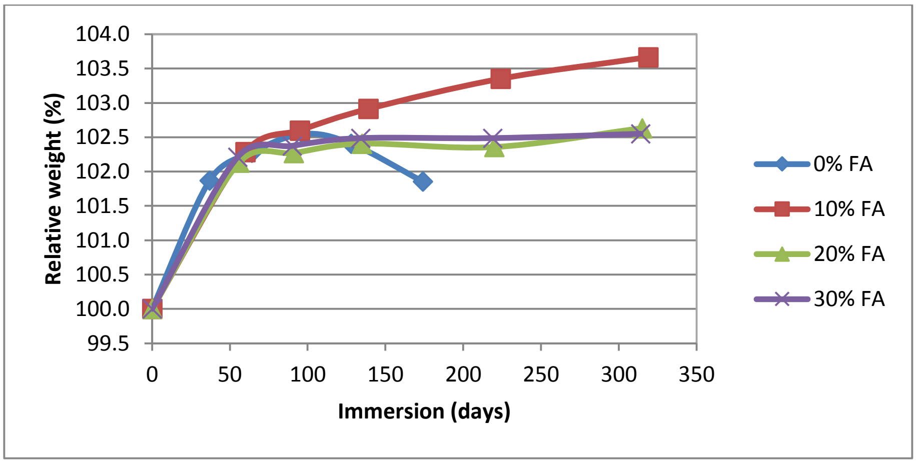


Figure 6.14: Relative weight of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio=0.8 in sulphate solution (Group 4).

Visual observation

The deterioration of the mortar mixes with different unprocessed fly ash content in sulphate solution is shown in Figure 6.15 and Figure 6.16. No significant changes due to sulphate attack were observed for mortar mixes with 30% unprocessed fly ash replacement during the entire immersion time (for both RSS contents). For mixes with RSS/Binder ratio of 0.65, no significant changes were observed for specimens with 20% unprocessed fly ash replacement until later ages, whereas the first sign of deterioration was seen on specimens with 10% unprocessed fly ash replacement at 217 days (Figure 6.15). For the mortar mixes with RSS/Binder ratio of 0.8, no significant changes due to sulphate attack were observed for specimens with 20% unprocessed fly ash replacement until later ages, whereas the first sign of deterioration that was seen on specimens with 10% unprocessed fly ash was at 90 days (Figure 6.16).

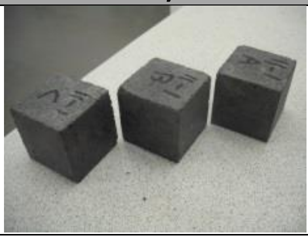
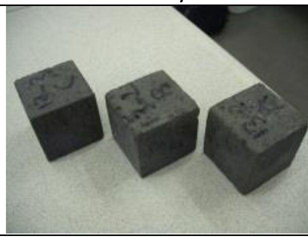
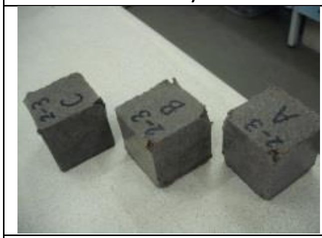
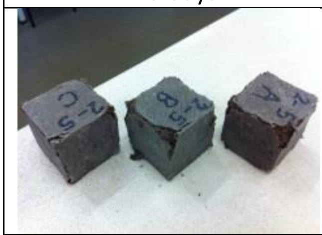
0% Fly ash	10% Fly ash	20% Fly ash	30% Fly ash
			
38 days	53 days	48 days	47 days
			
65 days	89 days	84 days	83 days
			
98 days	144 days	139 days	138 days
			
129 days	217 days	212 days	211 days
			
175 days	313 days	308 days	307 days

Figure 6.15 : Deterioration of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.65 in sulphate solution (Group 3).

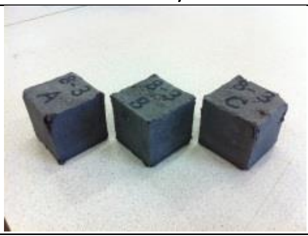
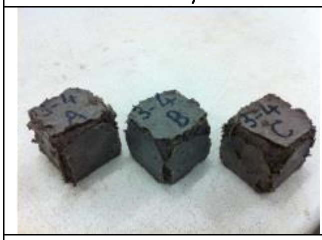
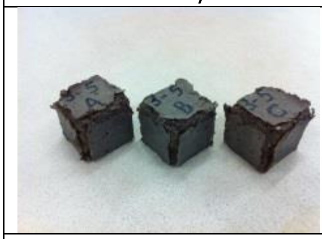
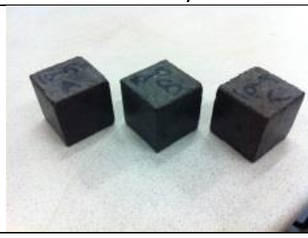
0% Fly ash	10% Fly ash	20% Fly ash	30% Fly ash
			
37 days	60 days	56 days	55 days
			
64 days	95 days	91 days	90 days
			
97 days	139 days	135 days	134 days
			
128 days	224 days	220 days	219 days
			
174 days	319 days	315 days	314 days

Figure 6.16 : Deterioration of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.8 in sulphate solution (Group 4).

6.4.1.3 Influence of fly ash in the control (Group 5)

Compressive strength

The compressive strength and relative strength of the control mixes with different unprocessed fly ash content are shown in Figure 6.17 and Figure 6.18. As the compressive strength of the mortar mixes with unprocessed fly ash continued to develop with immersion time and no signs of declining were observed, the results confirmed that the incorporation of unprocessed fly ash significantly improved long-term sulphate attack resistance. The greatest strength of 20.8 MPa was recorded for the mortar mix with 30% unprocessed fly ash at 300 days. The results also showed that the strength of the control mix without unprocessed fly ash developed quickly during the first 83 days of immersion prior to its subsequent falling at later ages. The relative strength results (Figure 6.18) confirmed the continual development in strength of the mortar mix with unprocessed fly ash.

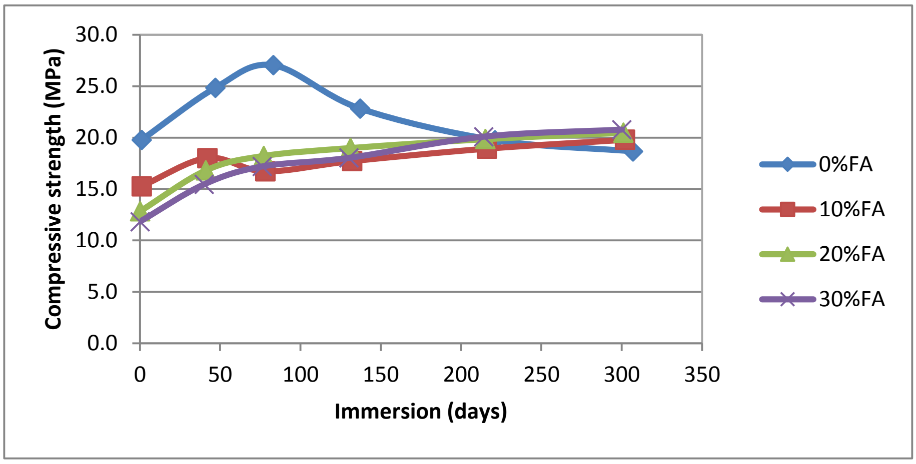


Figure 6.17: Compressive strength of the control mixes with different unprocessed fly ash content in sulphate solution (Group 5).

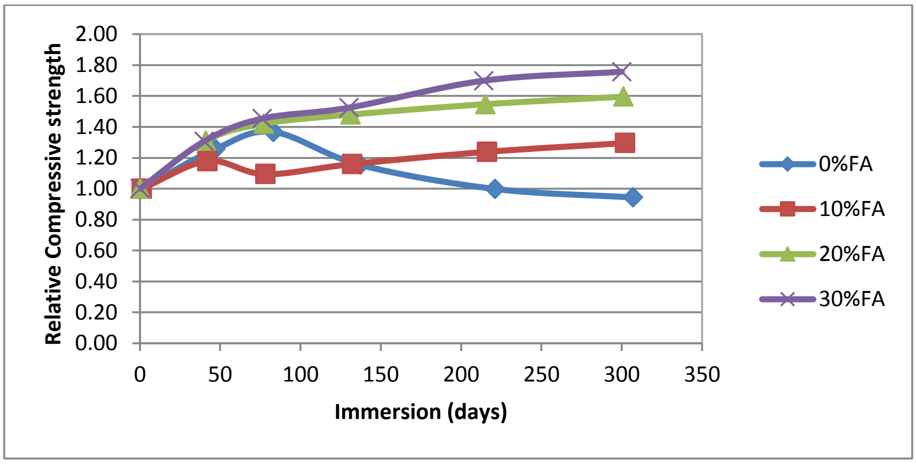


Figure 6.18 : Relative strength of the control mixes with different unprocessed fly ash content in sulphate solution (Group 5).

<u>Relative weight</u>

The relative weight of the control mixes with different unprocessed fly ash content (Groups 5) in sulphate solution is presented in Figure 6.19. The relative weight was recorded for the last three specimens in the sulphate solution for each mix. The relative weight was determined by dividing the weight of immersed samples by its original weight and then timed by 100%. The figure shows that the relative weight of the control mixes with unprocessed fly ash continued to increase during the first 90 days. Thereafter, the weight change was not significant. For the mortar mixes with RSS/Binder ratio of 0.8, the relative weight continued to develop during the first 50 days. Thereafter, the weight of the mortar mixes with 30% unprocessed fly ash replacement remained constant with less than 0.5% increase. The weight of the remaining mixes continued to increase with time.

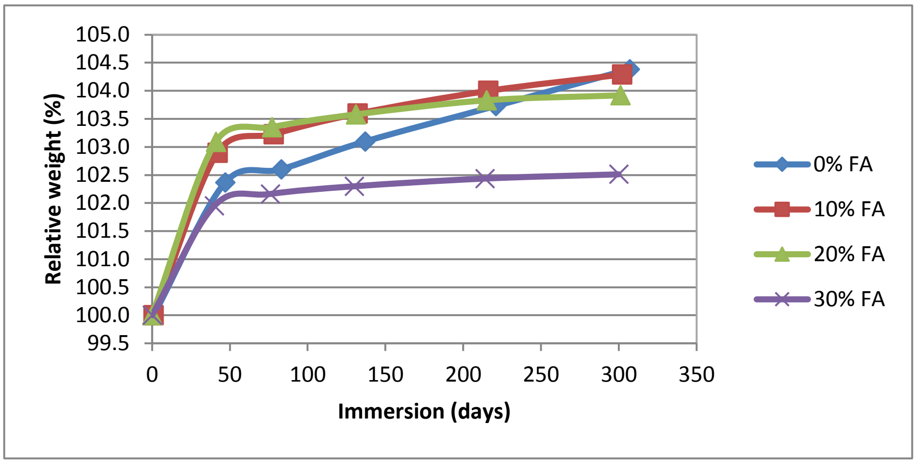


Figure 6.19: Relative weight of the control mixes with different unprocessed fly ash content in sulphate solution (Group 5).

<u>**Visual observation**</u>

The deterioration of the control mixes with different unprocessed fly ash content in sulphate solution is presented in Figure 6.20. The figure clearly shows that the addition of unprocessed fly ash significantly improved sulphate attack resistance, as no signs of deterioration were observed for all mortar mixes with unprocessed fly ash until later ages. For the mortar mix without unprocessed fly ash, the first sign of deterioration was observed at 137 days.

Figure 6.20: Deterioration of the control mixes with different fly content and Water/Binder ratio=0.8 in sulphate solution (Group 5).

6.4.2 Series 3: Concrete mixes with RSS and unprocessed fly ash

Compressive strength

The Compressive strength and relative strength of the concrete mixes with different unprocessed fly ash content in sulphate solution is shown Figure 6.21 and Figure 6.22. Figure 6.21 shows that the addition of unprocessed fly ash improved sulphate attack resistance and the best results of long-term compressive strength was recorded for the concrete mix with 20% unprocessed fly ash replacement. The figure also shows that the strength of concrete mixes with unprocessed fly ash continued to develop until later ages (except for the concrete mix with 15% unprocessed fly ash, which started to decline after 287 days). Figure 6.22 shows a rapid development in strength for the concrete mix without unprocessed fly ash during the first 42 days of immersion; however the strength started to decline noticeably afterwards. The results also showed a steady strength development for both concrete mixes with 10 and 20% unprocessed fly ash replacement. The control mix showed comparatively better resistance to sulphate attack than that made with RSS, as presented in Figure 6.23 and Figure 6.24.

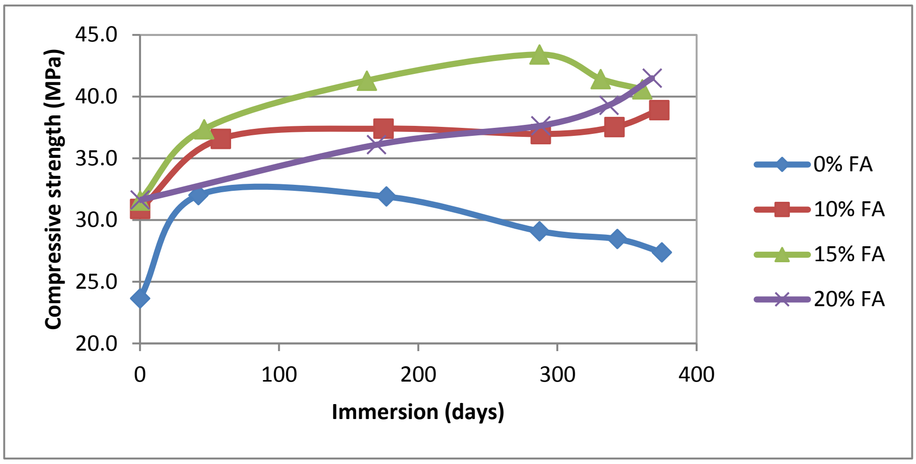


Figure 6.21: Compressive strength of concrete mixes sulphate solution (Series 3).

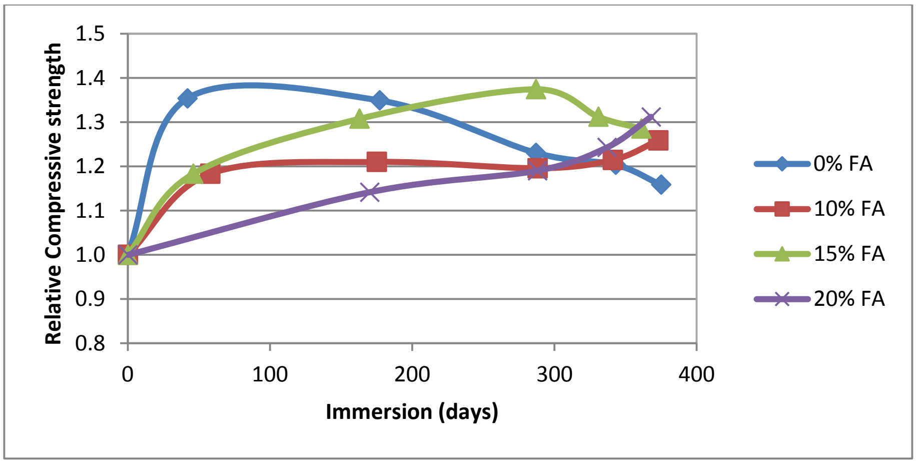


Figure 6.22: Relative strength of concrete mixes in sulphate solution (Series 3).

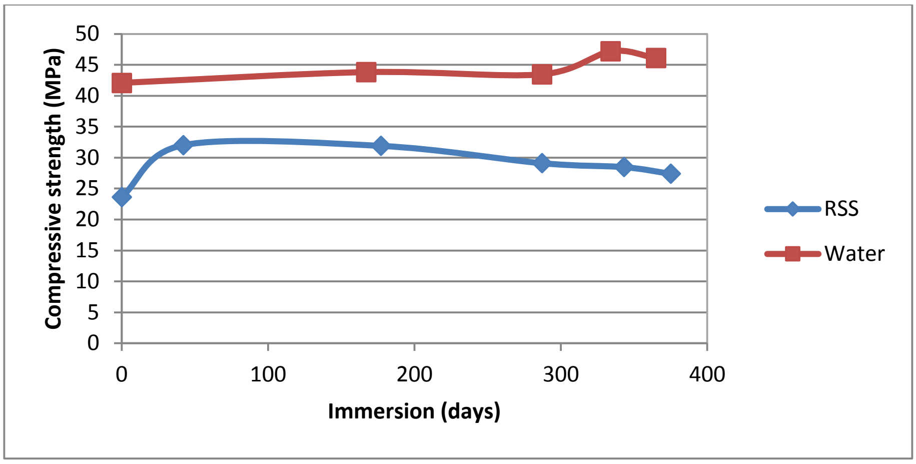


Figure 6.23: Compressive strength of concrete mixes with RSS and water in sulphate solution.

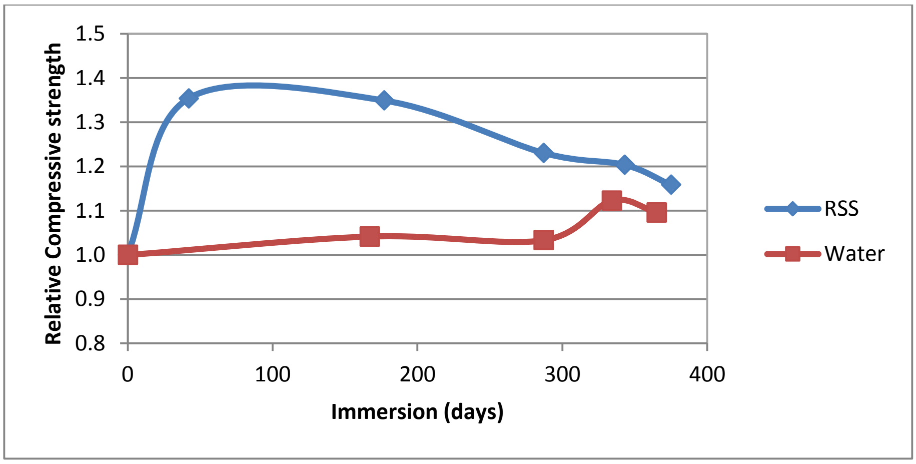


Figure 6.24: Relative strength of concrete mixes with RSS and water in sulphate solution.

Relative weight

The relative weight of the concrete mixes with different unprocessed fly ash content (Series 3) in sulphate solution is presented in Figure 6.25. The relative weight was recorded for the last two specimens in the sulphate solution for each mix. The relative weight was determined by dividing the weight of immersed samples by its original weight and then timed by 100%. The figure demonstrates that the relative weight increased during the first 50 days of immersion. Afterwards, no significant change in weight was observed for the concrete mixes with or without unprocessed fly ash. The relative weight of the concrete mixes with RSS and water is shown in Figure 6.27. The figure shows no significant difference in relative weight between the control mix and the one made with RSS.

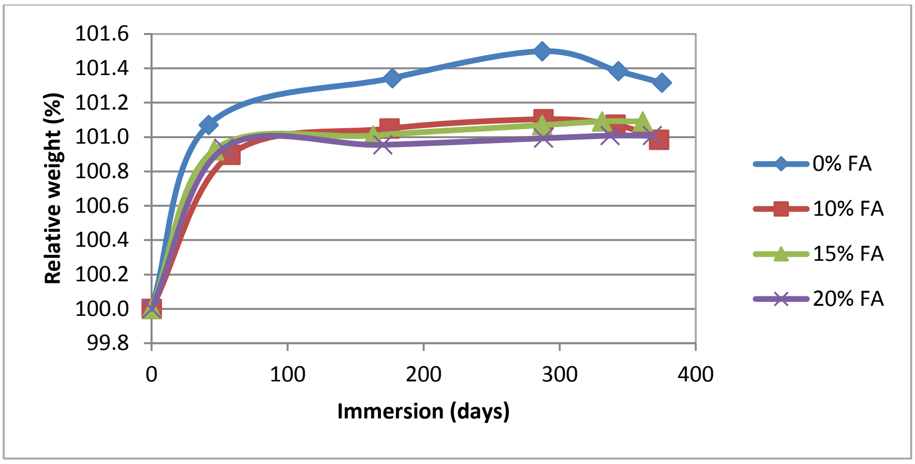


Figure 6.25: Relative weight of concrete mixes in sulphate solution (Series 3).

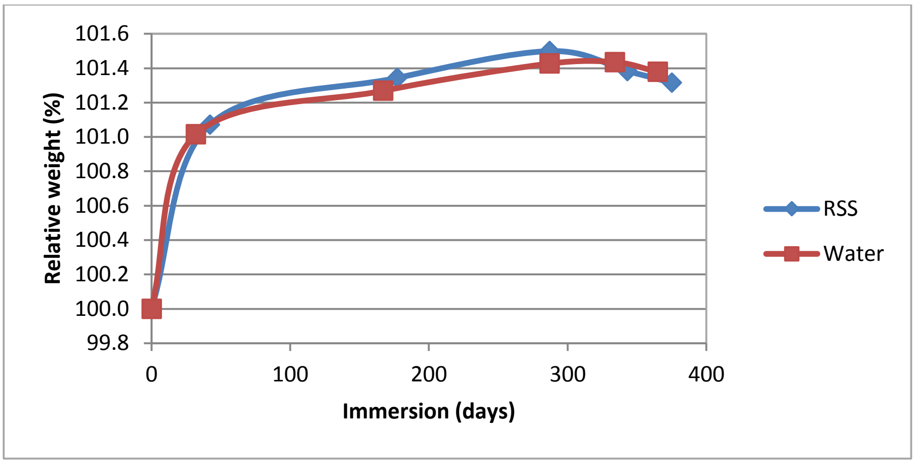


Figure 6.26: Relative weight of concrete mixes with RSS and water in sulphate solution.

Visual observation

The deterioration of concrete mixes with different unprocessed fly ash content in sulphate solution is shown in Figure 6.27. The figure clearly shows that the addition of unprocessed fly ash significantly improved sulphate attack resistance, as no clear changes were observed for the concrete mixes with unprocessed fly ash replacement until later ages. However, early signs of deterioration were observed at 288 days for the concrete mix with 10% unprocessed fly ash replacement. For the concrete mix without unprocessed fly ash the earliest signs of deterioration were observed at 287 days. The results also revealed that the control mix (made with water) showed comparatively better resistance to sulphate attack (Figure 6.28).

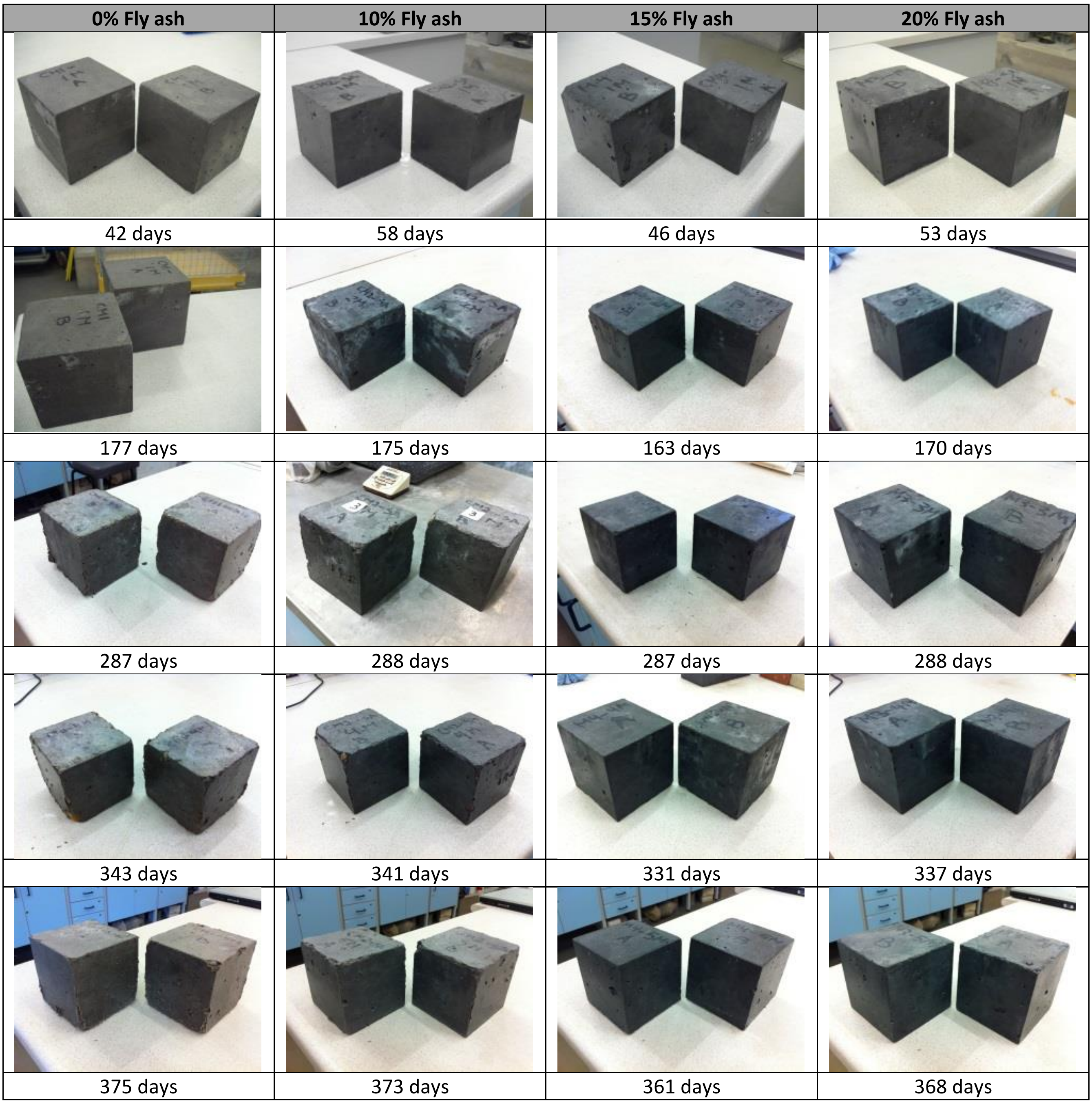


Figure 6.27: Deterioration of concrete specimens in sulphate solution (Series 3).

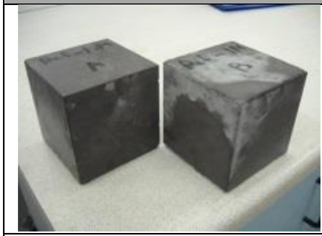
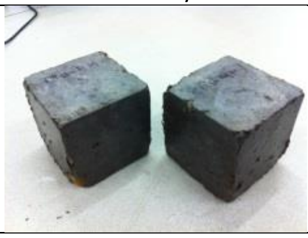
Water	RSS
	
32 days	42 days
	
167 days	177 days
	
287 days	287 days
	
334 days	343 days
	
365 days	375 days

Figure 6.28: Deterioration of concrete specimens with RSS and water in sulphate solution.

6.5 CONCLUSIONS

This chapter examined the resistant of cement-based systems that incorporated RSS and unprocessed fly ash to sulphate attack. Two series of cement-based materials were evaluated. Cement-based materials included mortar mixes with RSS and unprocessed fly ash (Series 1), and concrete mixes with RSS and unprocessed fly ash (Series 3). The main conclusions of this chapter are summarised below:

- Sulphate attack resistance of mortar mixes weakened when the content of the RSS increased. The best results were recorded for the mortar mix with RSS/Cement of 0.5 (M1).
- The sulphate resistance for both concrete and mortar mixes made with water was comparatively better than those made with RSS.
- The inclusion of unprocessed fly ash significantly improved sulphate attack resistance for both concrete and mortar mixes. The greater the amount of unprocessed fly ash the better the sulphate attack resistance. The best results were recorded when cement was replaced by 30% unprocessed fly ash for the mortar mixes and 20% unprocessed fly ash for concrete mix.

CHAPTER 7: ENVIRONMENTAL PROPERTIES-LEACHING TEST

7.1 INTRODUCTION

The environment refers to the sum total of human surroundings that consist of the atmosphere, the hydrosphere, the lithosphere and the biota (Radojevic and Bashkin, 1999). Human beings are significantly dependant on the environment to fulfil their life requirements including air, water and food. Environment also provides us with other raw materials that we need in the construction industry, for the production of numerous consumer goods, etc.

Analysing and monitoring the impact of different human activities on the environment is therefore essential in order to maintain safe surroundings and to provide high life quality. As both water and the atmosphere are the major routes for the dispersal of different pollutants, engineering professionals are consequently required to minimise the disturbance of these surroundings and to reduce pollution levels by considering innovative practices.

The examination of leaching properties of cement-based materials that incorporated waste products is vital in order to understand the leaching behaviour of different pollutants and to assess the safety of produced construction materials. Leaching properties provides a clearer image about the concentration of contaminants that potentially percolate into the surroundings, and gives engineering professionals the opportunity of proposing the most effective solutions that may be necessary to mitigate any associated risks.

7.2 AIMS AND OBJECTIVES

The aim of this chapter is to evaluate the leaching properties of cement-based materials incorporating RSS and unprocessed fly ash. 17 mortar mixes (Series 1) that incorporated RSS and unprocessed fly ash were assessed. Leaching test was performed on mortar specimens to evaluate their effectiveness in detaining pollutants that were originally presented in both RSS and unprocessed fly ash. Pollutants included heavy metals and free ions.

This chapter aimed to determine the concentration of different pollutants (presented in both RSS and unprocessed fly ash) that percolated into the test leachant, and to compare them with the requirements of a number of EU water standards/directives. This comparison will provide a clearer image about the quality of the water that was in direct contact with the test specimens, and consequently assess the impact of using RSS and unprocessed fly ash in cement-based materials on the surrounding environment.

7.3 MATERIALS, MIXING PROPORTIONS, PREPARATIONS AND TESTING

Mortar samples were prepared using different construction materials including Portland cement, fine aggregate, coarse aggregate, drinking water, Raw Sewage Sludge (RSS) and unprocessed fly ash. Mixing Proportions

Series 1 was only used to perform leaching Test, which consisted of 17 mortar mixes that mainly incorporated a constant sand to binder ratio of 4.5 with different liquid to binder ratios (0.5, 0.65, 0.8 and 1). Unprocessed fly ash was used as a cement replacement at four different proportions of 0, 10, 20 and 30% of total binder weight. The last four mixes in this series were made with drinking water (Water/Binder ratio of 0.8) and considered as the control. More details about mixes composition can be found in Section 3.3.10.

Mortar samples were prepared and compacted manually in accordance to ASTM C109/C109M-02 (ASTM, 2008) using 50mm in size steel moulds. Cast specimens were covered with plastic sheets and placed in a room at a temperature of 20^{o}C for 24 hours until demoulding. Thereafter, samples were wrapped by a cling film until testing. Two mortar specimens were used for leaching test, which was carried out in accordance to Draft BS EN 15863:2008 (BSI, 2008b). Specimens were cured for 28 days and were later used to perform leaching test as described in Section 3.5.9.

7.4 RESULTS

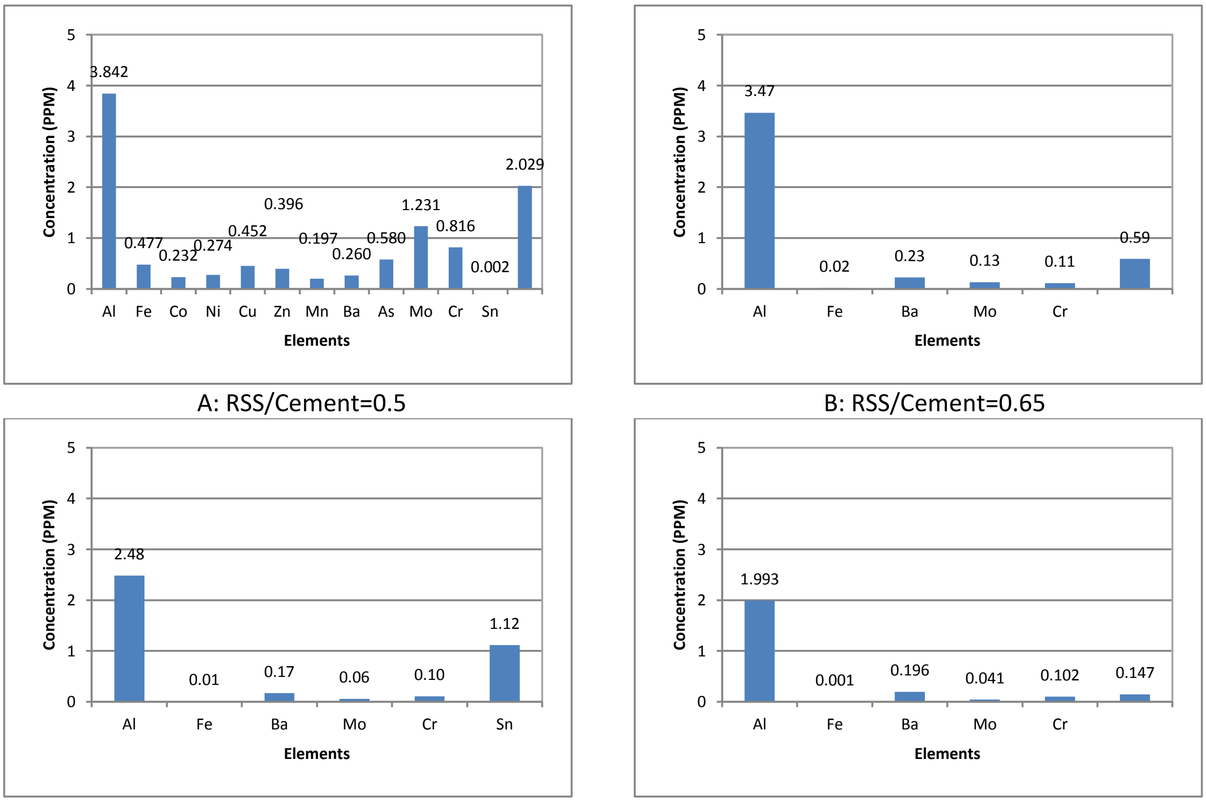
7.4.1 Influence of RSS (Group 1)

<u>Heavy metals</u>

Table 7.1 and Figure 7.1 show the leaching properties for mortar specimens with different RSS content. This group included four mortar mixes (M1, M2, M3 and M4) that incorporated a constant sand to cement ratio of 4.5, 0% unprocessed fly ash and four RSS/Cement ratios of 0.5, 0.65, 0.8 & 1. For comparison purposes, M14 (which contained drinking water equivalent to the water content of M3), was also tested as the control. The results showed that the concentration of detected heavy metals were mostly below 1 PPM. However, the results showed higher concentrations of some elements including Al, Mo and Sn, and the greatest recorded concentrations of the above elements were 3.84, 1.23, 2.03 PPM respectively for M1 (RSS/Cement ratio of 0.5). The results also showed that the concentration of detected heavy metals for the mortar mix made with water were generally less than those of the mix made with RSS (Table 7.2 and Figure 7.2).

Table 7.1: Heavy metals concentration of mortar specimens with different RSS content (PPM).

Metal	RSS/C=0.5			RSS/C=0.65			RSS/C=0.8			RSS/C=1		
	2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Al	0.36	1.84	3.84	0.02	1.64	3.47	0.00	0.73	2.48	0.00	0.40	1.99
Fe	0.07	0.46	0.48	0.01	0.02	0.02	0.00	0.01	0.01	0.00	0.00	0.00
Co	0.03	0.23	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.06	0.25	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.04	0.45	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.02	0.40	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.06	0.20	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.22	0.26	0.00	0.13	0.23	0.00	0.12	0.17	0.00	0.13	0.20
Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As	0.37	0.57	0.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mo	0.60	1.07	1.23	0.06	0.12	0.13	0.01	0.06	0.06	0.00	0.04	0.04
Cr	0.23	0.78	0.82	0.11	0.11	0.11	0.10	0.10	0.10	0.10	0.10	0.10
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn	1.25	2.03	2.03	0.34	0.59	0.59	0.34	1.12	1.12	0.15	0.15	0.15



A: RSS/Cement=0.5

B: RSS/Cement=0.65

C: RSS/Cement=0.8

D: RSS/Cement=1

Figure 7.1: Total heavy metals concentration (28 days) of mortar specimens with different RSS content in PPM.

Table 7.2: Heavy metals concentration of mortar specimens with different liquid type (PPM).

Metal	RSS			Water		
	2H	8D	28D	2H	8D	28D
Al	0.00	0.73	2.48	0.05	0.32	0.89
Fe	0.00	0.01	0.01	0.00	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.12	0.17	0.00	0.00	0.00
Se	0.00	0.00	0.00	0.00	0.00	0.00
As	0.00	0.00	0.00	0.00	0.00	0.00
Mo	0.01	0.06	0.06	0.00	0.00	0.00
Cr	0.10	0.10	0.10	0.00	0.00	0.00
Pb	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.34	1.12	1.12	0.00	0.00	0.00

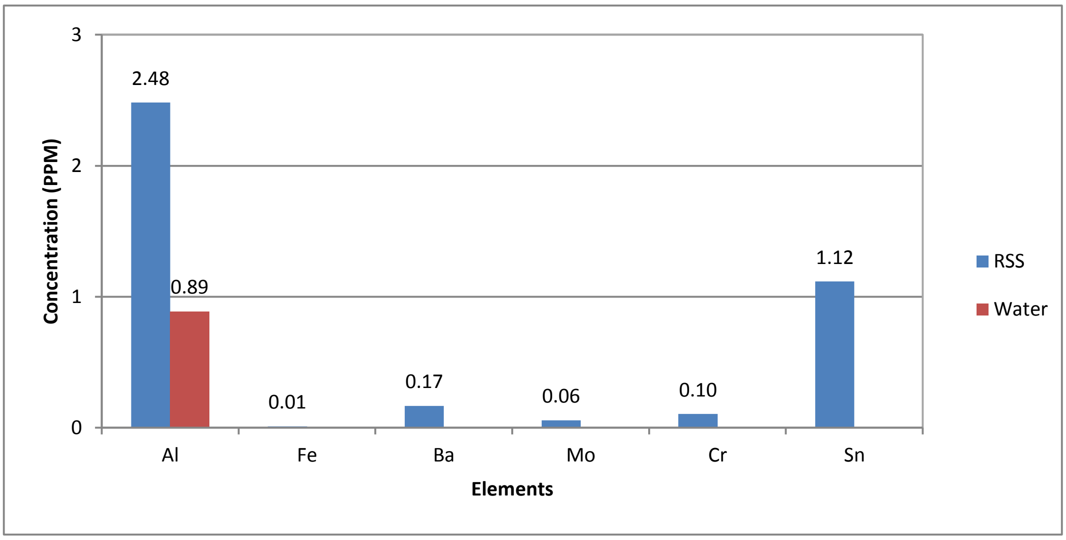


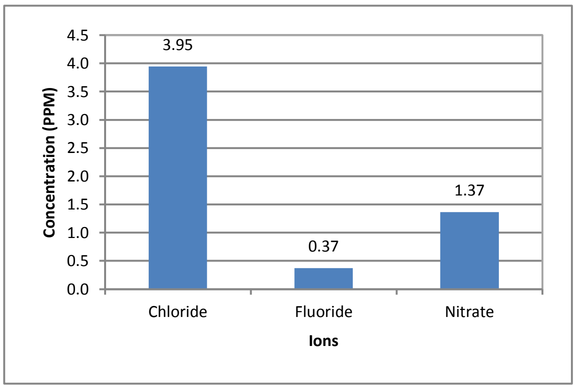
Figure 7.2: Total heavy metals concentration (28 days) of mortar specimens with different liquid type (PPM).

Ion Chromatography System analysis

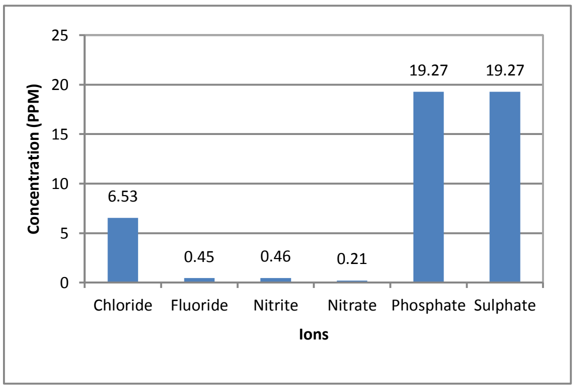
The Ion Chromatography System analysis for Group 1 is presented in Table 7.3 and Figure 7.3. The results showed that the concentration of detected ions was relatively low and mostly below 2 PPM. However some ions showed higher concentrations and this included Cl^-, PO_4^{3-} and HSO_4^-. The greater concentration of 19.72 PPM was recorded for PO_4^{3-} for the mortar mix with RSS/Cement ratio of 0.6 (M2), and the other high concentration of 19.21 PPM was recorded for Cl^- for the mortar mix with RSS/Cement ratio of 0.8 (M3). The results also showed that concentrations of both Cl^- and HSO_4^- were comparatively higher in the mortar mix made with RSS than that made with water (Table 7.4 and Figure 7.4).

Table 7.3: Ion analysis of mortar mixes with different RSS content (PPM).

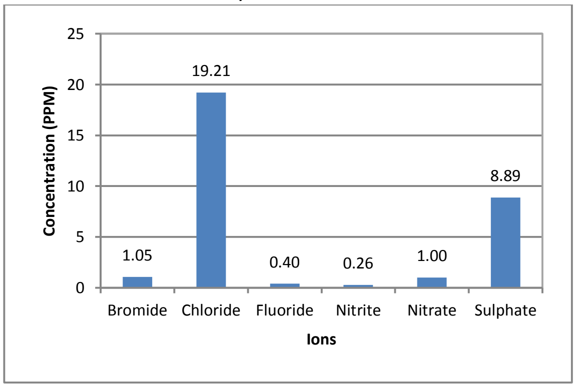
Ion	Formula	RSS/C=0.5			RSS/C=0.65			RSS/C=0.8			RSS/C=1		
		2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Bromide	Br^-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.05	0.00	0.00	0.26
Chloride	Cl^-	1.57	2.45	3.95	1.29	1.96	6.53	0.94	2.00	19.21	0.26	1.00	2.60
Fluoride	F^-	0.00	0.23	0.37	0.00	0.24	0.45	0.00	0.22	0.40	0.00	0.22	0.38
Nitrite	NO_2^-	0.00	0.00	0.00	0.00	0.25	0.46	0.00	0.00	0.26	0.00	0.00	0.24
Nitrate	NO_3^-	0.00	0.54	1.37	0.00	0.00	0.21	0.00	1.00	1.00	0.00	0.50	1.38
Phosphate	PO_4^{3-}	0.00	0.00	0.00	19.27	19.27	19.27	0.00	0.00	0.00	0.00	0.00	0.00
Sulphate	SO_4^{-2}	0.00	0.00	0.00	1.86	2.01	19.27	5.49	7.54	8.89	0.51	1.10	2.28



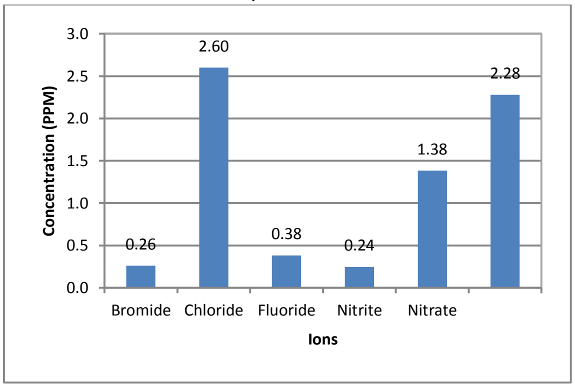
A: RSS/Cement=0.5



B: RSS/Cement=0.65



C: RSS/Cement=0.8



D: RSS/Cement=1

Figure 7.3: Total ions concentration (28 days) of mortar mixes with different RSS content (PPM).

Table 7.4: Ion analysis of mortar specimens with different liquid type (PPM).

Ion	Formula	RSS			Water		
		2H	8D	28D	2H	8D	28D
Bromide	Br^-	0.00	0.00	1.05	0.00	0.00	0.00
Chloride	Cl^-	0.94	2.00	19.21	0.79	3.57	8.22
Fluoride	F^-	0.00	0.22	0.40	0.00	0.00	0.00
Nitrite	NO_2^-	0.00	0.00	0.26	0.00	0.00	0.00
Nitrate	NO_3^-	0.00	1.00	1.00	0.96	4.25	5.48
Phosphate	PO_4^{3-}	0.00	0.00	0.00	0.38	0.38	0.38
Sulphate	SO_4^{-2}	5.49	7.54	8.89	1.90	3.49	7.60

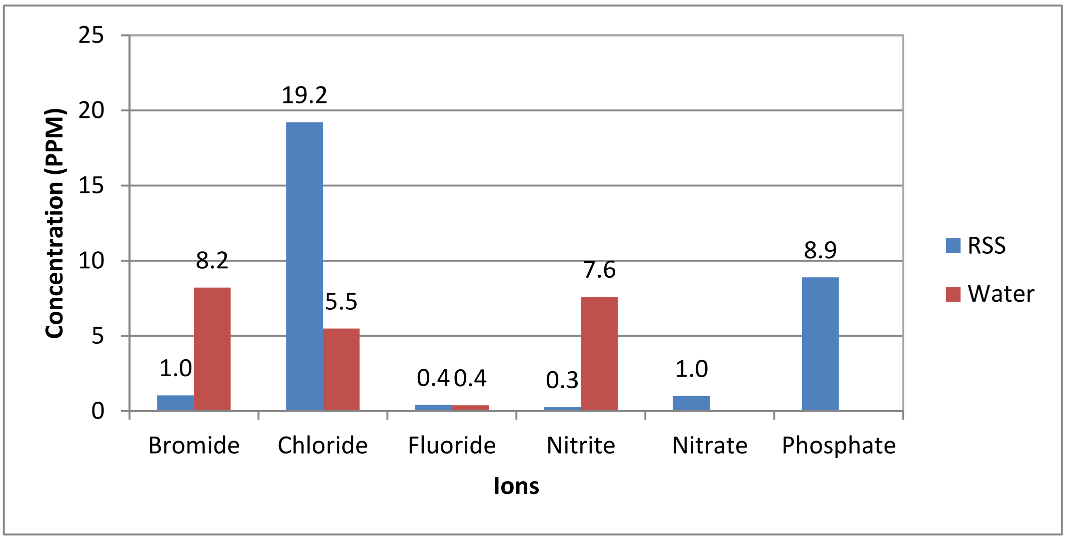


Figure 7.4: Total ions concentration (28 days) of mortar specimens with different liquid type in PPM.

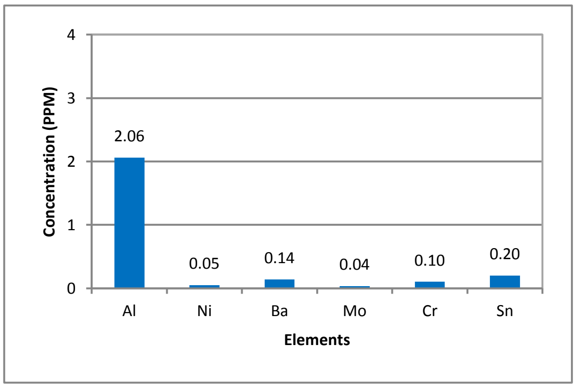
7.4.2 Influence of sand content (Group 2)

Heavy metals

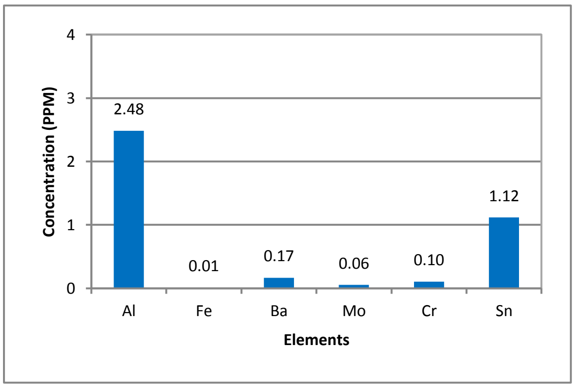
The influence of varying sand content on leaching properties of mortar specimens is shown in Table 7.5 and Figure 7.5. This group included four mixes that contained a constant RSS/Cement ratio of 0.8 and four sand to cement ratios of 3, 4.5, 6 and 7.5 (for M5, M3, M6 and M7 respectively). The results showed that the concentrations of detected heavy metals were mostly below 1 PPM. However, the results showed higher concentrations of some elements including Al and Sn, and the greatest recorded concentrations were 3.1 PPM of Al for the mortar mix with sand to cement content of 7.5 (M7), and 1.12 PPM of Sn for the mortar mix with sand to cement ratio of 4.5 (M3).

Table 7.5: Heavy metals concentration of mortar specimens with different sand content (Group 2) in PPM.

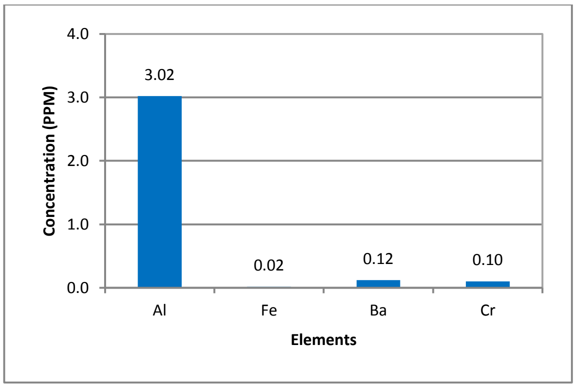
Metal	Sand to cement ratio=3			Sand to cement ratio=4.5			Sand to cement ratio=6			Sand to cement ratio=7.5		
	2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Al	0.02	0.29	2.06	0.00	0.73	2.48	0.01	0.93	3.02	0.02	1.12	3.10
Fe	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.02	0.02	0.00	0.01	0.01
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.08	0.14	0.00	0.12	0.17	0.00	0.08	0.12	0.00	0.06	0.08
Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mo	0.00	0.04	0.04	0.01	0.06	0.06	0.00	0.00	0.00	0.00	0.03	0.03
Cr	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.20	0.20	0.20	0.34	1.12	1.12	0.00	0.00	0.00	0.06	0.06	0.06



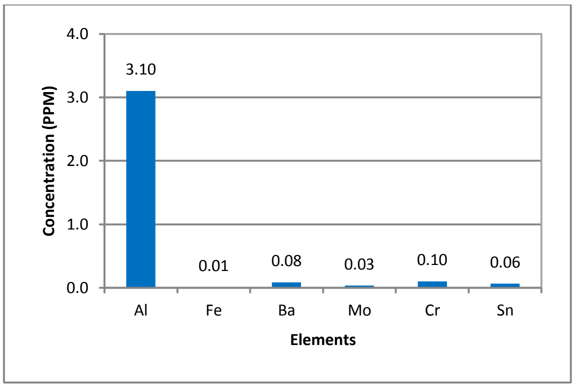
A: Sand to cement ratio of 3



B: Sand to cement ratio of 4.5



C: Sand to cement ratio of 6



D: Sand to cement ratio of 7.5

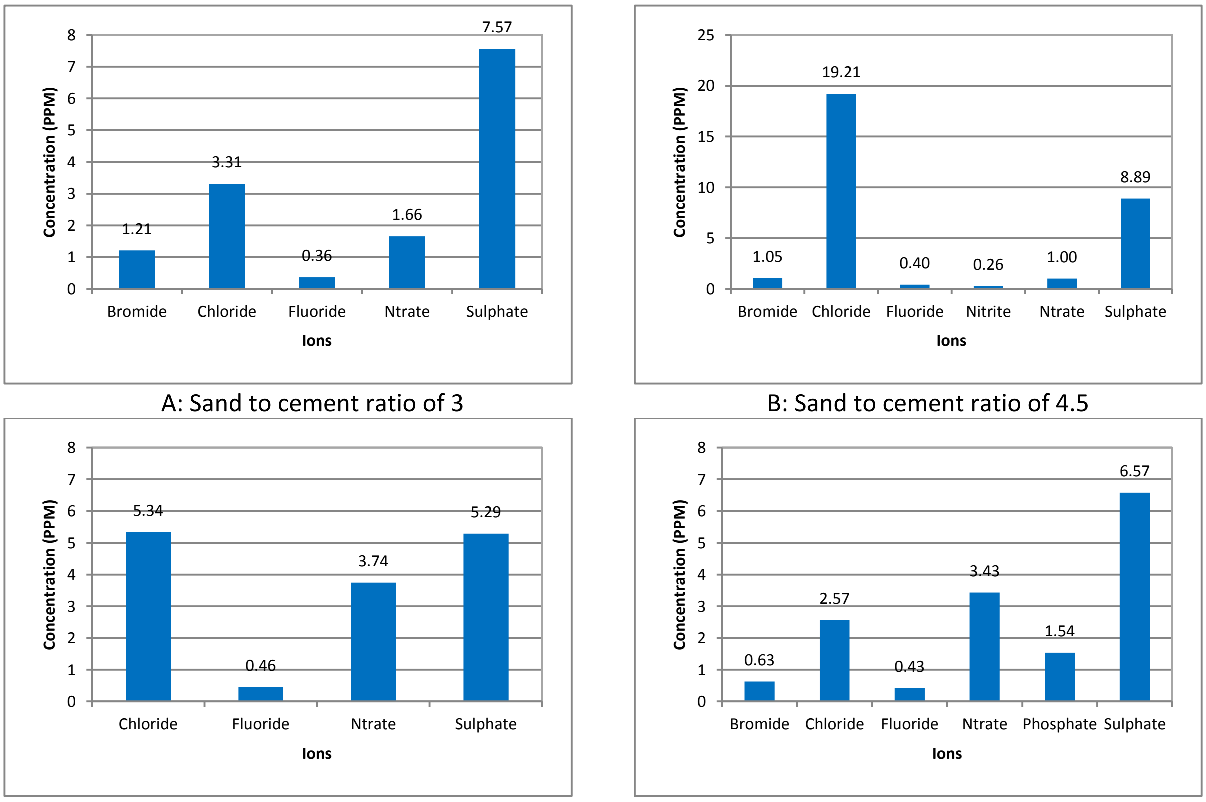
Figure 7.5: Total heavy metals concentration (28 days) of mortar specimens with different sand content (PPM).

The Ion Chromatography System analysis

The Ion Chromatography System analysis for mortar mixes with different sand content is shown in Table 7.6 and Figure 7.6. The concentration of detected ions was relatively low and mostly below 2 PPM. However the results showed higher concentrations of some ions including Cl^- and HSO_4^-. The greatest concentrations of 19.21 and 8.89 PPM of Cl^- & HSO_4^- respectively was recorded for the mortar mix with sand to cement ratio of 4.5 (M3).

Table 7.6: Ion analysis of mortar specimens with different sand content (PPM).

Ion	Formula	C:S=1:3			C:S=1:4.5			C:S=1:6			C:S=1:7.5		
		2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Bromide	Br^-	1.21	1.21	1.21	0.00	0.00	1.05	0.00	0.00	0.00	0.00	0.00	0.63
Chloride	Cl^-	0.67	1.69	3.31	0.94	2.00	19.21	1.19	1.88	5.34	0.37	1.53	2.57
Fluoride	F^-	0.00	0.23	0.36	0.00	0.22	0.40	0.00	0.23	0.46	0.00	0.17	0.43
Nitrite	NO_2^-	0.00	0.00	0.00	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.00	0.00
Nitrate	NO_3^-	0.00	0.97	1.66	0.00	1.00	1.00	0.00	0.88	3.74	0.00	1.60	3.43
Phosphate	PO_4^{3-}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.54	1.54	1.54
Sulphate	SO_4^{-2}	3.71	6.08	7.57	5.49	7.54	8.89	2.09	2.97	5.29	1.06	3.72	6.57



A: Sand to cement ratio of 3

B: Sand to cement ratio of 4.5

C: Sand to cement ratio of 6

D: Sand to cement ratio of 7.5

Figure 7.6: Total ions concentration (28 days) of mortar specimens with different sand content (PPM).

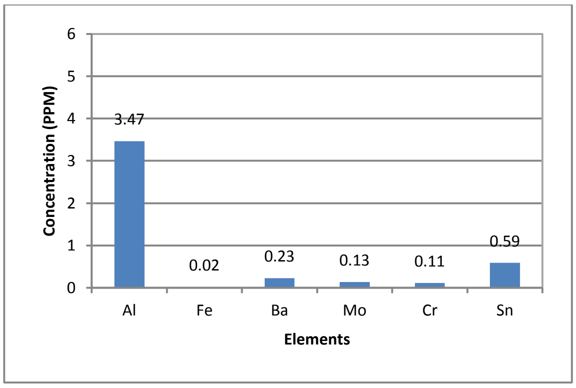
7.4.3 Influence of fly ash (Groups 3 and 4)

Heavy metals

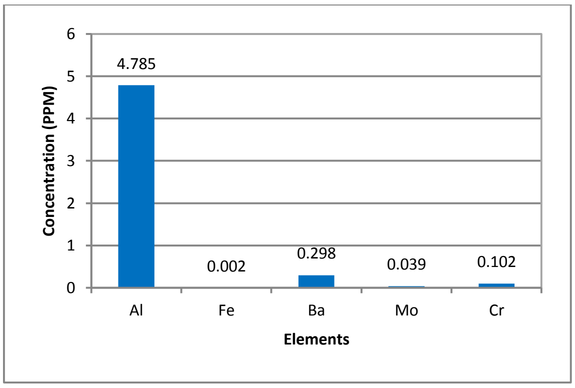
Leaching properties of heavy metals for mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3) are shown in Table 7.7 and Figure 7.7. For Group 4 (RSS/Binder ratio of 0.8) the results are presented in Table 7.8 and Figure 7.8. Two groups of mortar mixes, that contained a constant sand to binder ratio of 4.5 and four proportions of unprocessed fly ash (0, 10, 20 and 30% of total binder weight), were examined. Group 3 (M2, M11, M12 and M13) was prepared with RSS/Binder ratio of 0.65 whereas Group 4 (M3, M8, M9 and M10) was prepared with RSS/Binder ratio of 0.8. For Group 3, the results showed that the concentrations of detected heavy metals were mostly below 1 PPM, except Cu for M12 (20% unprocessed fly ash replacement). However, higher levels of Al concentrations were recorded for all mixes in this group. It was also noted that Al concentration increased when the content of unprocessed fly ash increased and the greatest Al concentration of 5.34 PPM was recorded for the mortar mix with 30% unprocessed fly ash (M13). For Group 4, the concentrations of detected heavy metals were mostly below 1 PPM, except Sn for the mix with 0% unprocessed fly ash (M2) and for 30% unprocessed fly ash (M13). However, higher levels of Al concentrations were recorded for all mixes in this group. It was also noted that Al concentration increased when the content of unprocessed fly ash was increased and the greatest Al concentration of 5.13 PPM was recorded for the mortar mix with 30% unprocessed fly ash (M13). No significant differences in heavy metal concentration were observed when RSS content was increased.

Table 7.7: Heavy metals concentration of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3) in PPM.

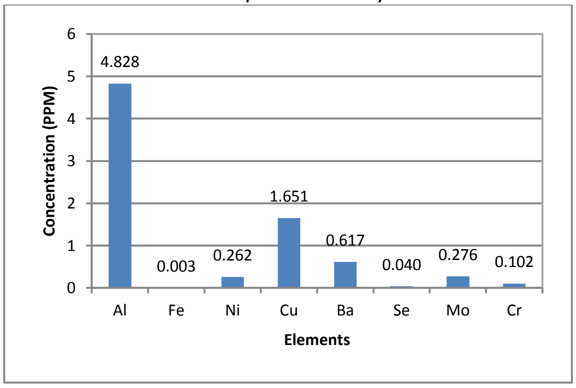
Metal	Fly ash=0%			Fly ash=10%			Fly ash=20%			Fly ash=30%		
	2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Al	0.02	1.64	3.47	0.01	2.78	4.79	0.03	2.83	4.83	0.05	2.29	5.34
Fe	0.01	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.65	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.13	0.23	0.00	0.17	0.30	0.00	0.17	0.62	0.00	0.09	0.14
Se	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.04	0.00	0.00	0.00
As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mo	0.06	0.12	0.13	0.00	0.04	0.04	0.00	0.04	0.28	0.00	0.03	0.03
Cr	0.11	0.11	0.11	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.34	0.59	0.59	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.75	0.75



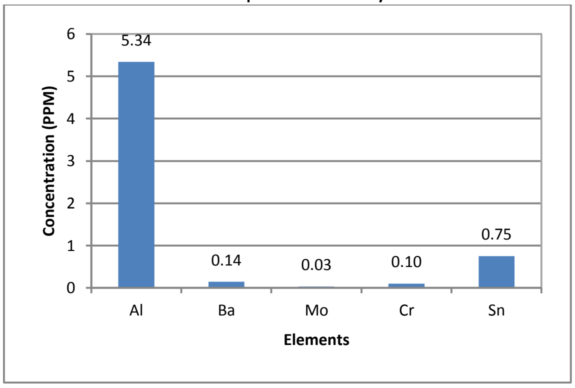
A: 0% unprocessed fly ash



B: 10% unprocessed fly ash



C: 20% unprocessed fly ash

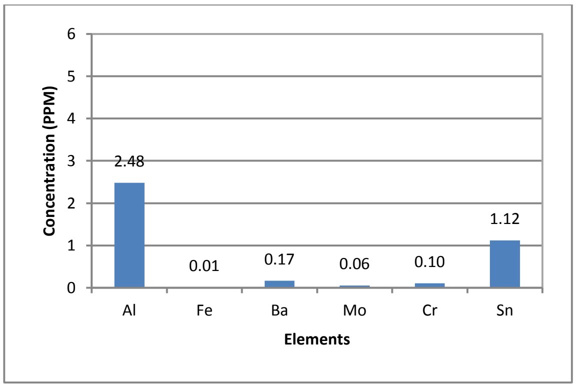


D: 0% unprocessed fly ash

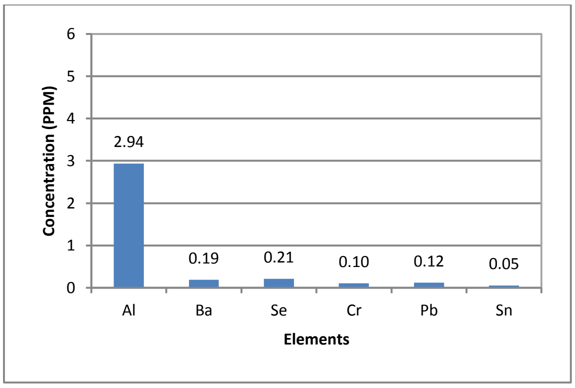
Figure 7.7: Total heavy metals concentration (28 days) of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3) in PPM.

Table 7.8: Heavy metals concentration of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4) in PPM.

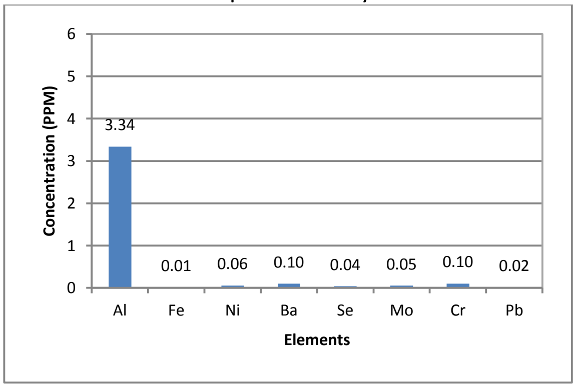
Metal	Fly ash=0%			Fly ash=10%			Fly ash=20%			Fly ash=30%		
	2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Al	0.00	0.73	2.48	0.00	0.84	2.94	0.04	0.66	3.34	0.05	2.03	5.13
Fe	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.06	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.12	0.17	0.00	0.14	0.19	0.00	0.07	0.10	0.00	0.17	0.19
Se	0.00	0.00	0.00	0.21	0.21	0.21	0.00	0.04	0.04	0.00	0.00	0.00
As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mo	0.01	0.06	0.06	0.00	0.00	0.00	0.00	0.05	0.05	0.00	0.04	0.04
Cr	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Pb	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.02	0.00	0.00	0.00
Sn	0.34	1.12	1.12	0.05	0.05	0.05	0.00	0.00	0.00	0.01	2.22	2.22



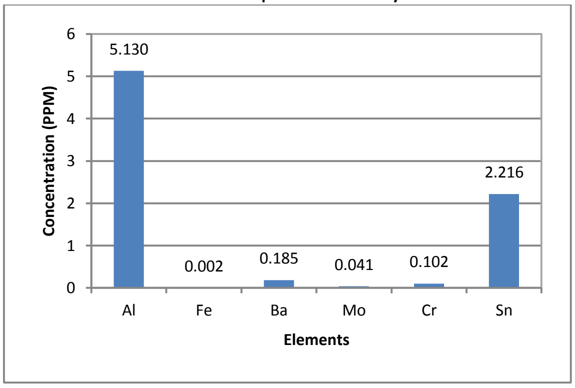
A: 0% unprocessed fly ash



B: 10% unprocessed fly ash



C: 20% unprocessed fly ash



D: 0% unprocessed fly ash

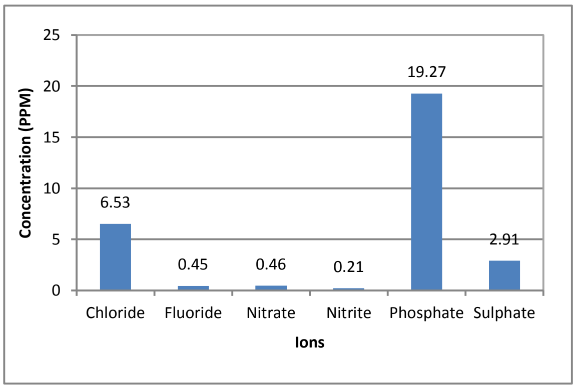
Figure 7.8: Total heavy metals concentration (28 days) of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4) in PPM.

<u>The Ion Chromatography System</u>

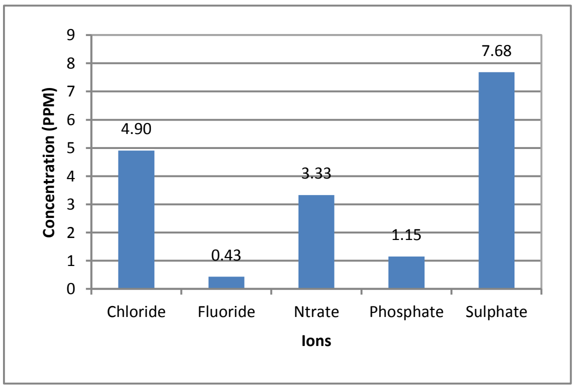
The Ion Chromatography System analysis for the mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3) is shown in Table 7.9 and Figure 7.9. The results for Group 4 (RSS/Binder ratio of 0.8) are presented in Table 7.10 and Figure 7.10. For Group 3, the results showed that the concentration of detected ions was relatively low and mostly below 2 PPM. However results showed higher concentrations of a number of ions including Cl- , NO3-, PO43- & HSO4-. The greatest ion concentrations were recorded as follows; 10.85 and 9.47 PPM of Cl- and HSO4- respectively for the mortar mix with 30% unprocessed fly ash (M13) and 19.27 PPM of PO43- for the mortar mix with 0% unprocessed fly ash (M2). For the mortar mixes with RSS/Binder ratio of 0.8 (Group 4), low concentration of Br-, F-, NO2- and PO43- (between 0-3.34 PPM) and higher concentration of Cl- , NO3- & HSO4- (between 4.1-19.21 PPM) were detected. The greatest concentration of ions were recorded as follows; 19.21 PPM of Cl- for the mortar mix with 0% unprocessed fly ash (M3), 4.1 PPM of NO3- for the mortar mix with 10% unprocessed fly ash (M8) , and 15.71 PPM of HSO4- for the mortar mix with 30% unprocessed fly ash (M10).

Table 7.9: Ion analysis of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3) in PPM.

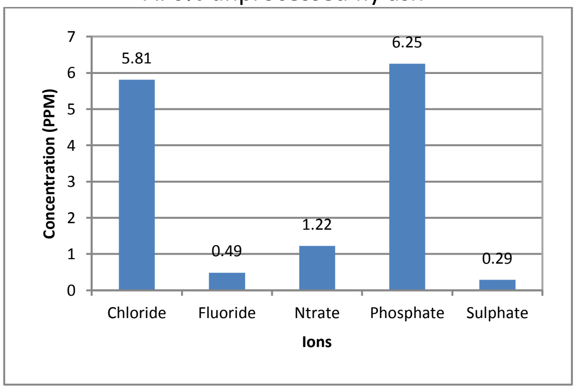
Ion	Formula	Fly ash=0%			Fly ash=10%			Fly ash=20%			Fly ash=30%		
		2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Bromide	Br^-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26
Chloride	Cl^-	1.29	1.96	6.53	2.88	3.49	4.90	1.41	2.02	5.81	0.89	1.80	10.85
Fluoride	F^-	0.00	0.24	0.45	0.00	0.24	0.43	0.00	0.24	0.49	0.00	0.15	0.31
Nitrite	NO_2^-	0.00	0.25	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nitrate	NO_3^-	0.00	0.00	0.21	0.00	0.39	3.33	0.00	0.39	1.22	0.00	1.40	6.16
Phosphate	PO_4^{3-}	19.27	19.27	19.27	1.15	1.15	1.15	2.37	2.37	6.25	0.00	0.00	0.00
Sulphate	SO_4^{-2}	1.86	2.01	2.91	6.40	6.69	7.68	0.00	0.29	0.29	2.38	4.91	9.47



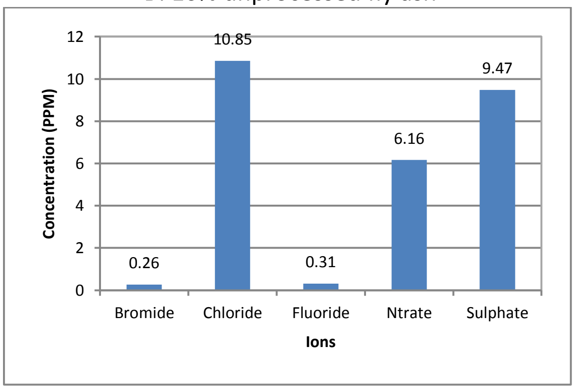
A: 0% unprocessed fly ash



B: 10% unprocessed fly ash



C: 20% unprocessed fly ash

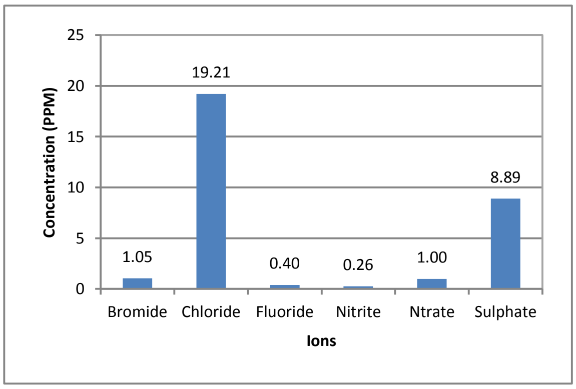


D: 0% unprocessed fly ash

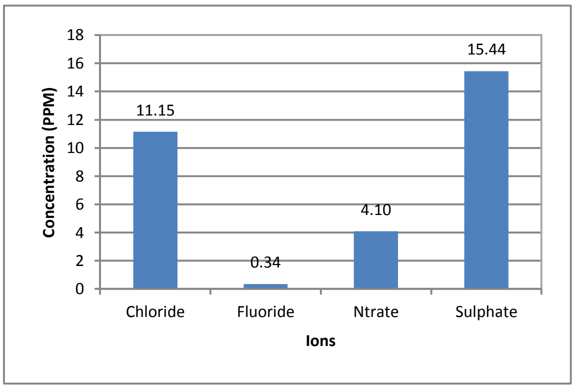
Figure 7.9: Total ions concentration (28 days) of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3) in PPM.

Table 7.10: Ion analysis of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4) in PPM.

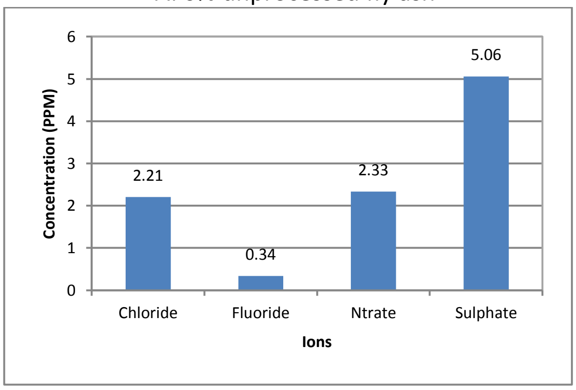
Ion	Formula	Fly ash=0%			Fly ash=10%			Fly ash=20%			Fly ash=30%		
		2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Bromide	Br^-	0.00	0.00	1.05	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.46	0.46
Chloride	Cl^-	0.94	2.00	19.21	2.87	9.49	11.15	0.34	0.95	2.21	3.77	4.93	6.39
Fluoride	F^-	0.00	0.22	0.40	0.00	0.20	0.34	0.00	0.19	0.34	0.37	0.53	0.68
Nitrite	NO_2^-	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.43	3.34
Nitrate	NO_3^-	0.00	1.00	1.00	0.00	2.77	4.10	0.00	0.37	2.33	0.00	0.16	0.16
Phosphate	PO_4^{3-}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sulphate	SO_4^{-2}	5.49	7.54	8.89	2.71	13.18	15.44	1.02	2.32	5.06	9.41	12.08	15.71



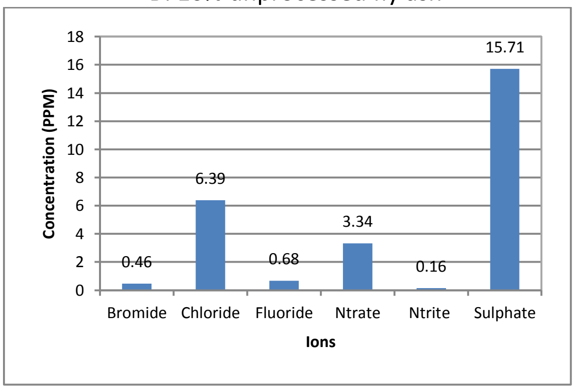
A: 0% unprocessed fly ash



B: 10% unprocessed fly ash



C: 20% unprocessed fly ash



D: 30% unprocessed fly ash

Figure 7.10: Total ions concentration (28 days) of mortar specimens with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4) in PPM.

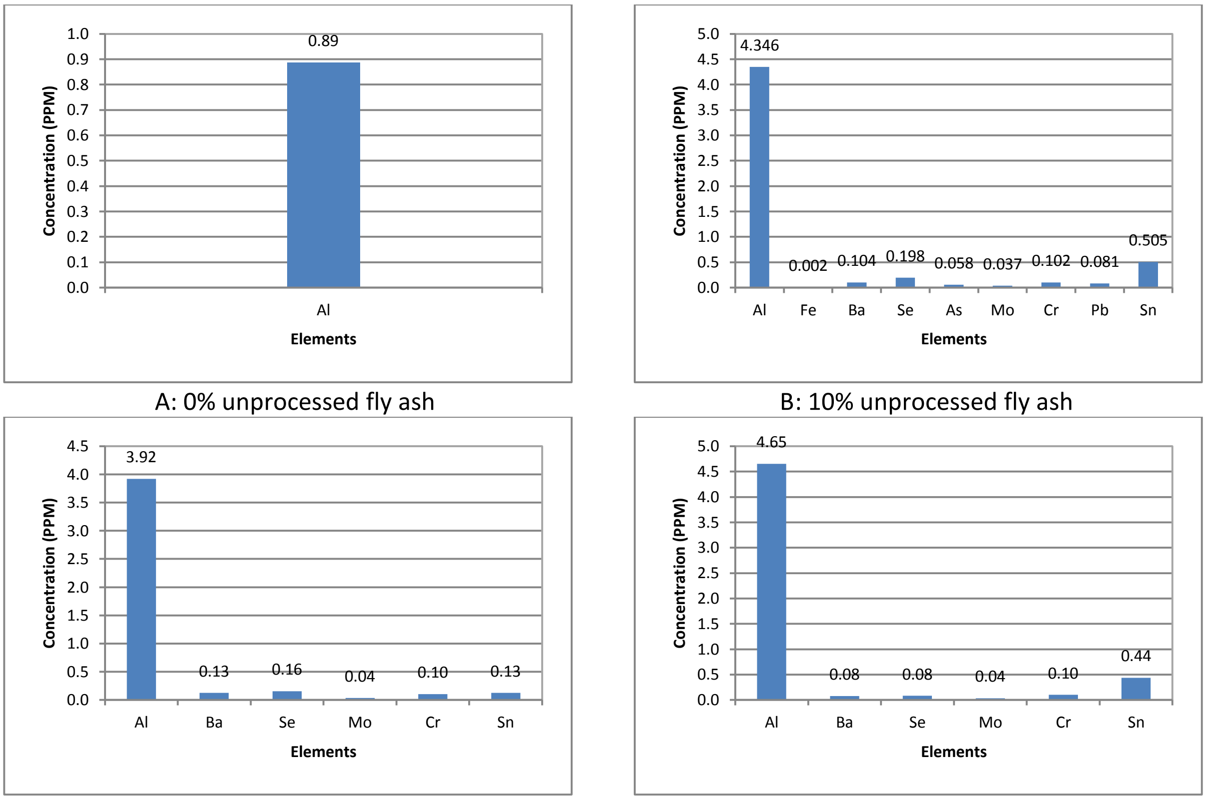
7.4.4 Influence of fly ash in the control (Group 5)

Heavy metals

Leaching properties of heavy metals for the control mixes is shown in Table 7.11 and Figure 7.11. Group 5 (M14, M15, M16 and M17) contained a constant sand to binder ratio of 4.5, Water/Binder ratio of 0.8 and four proportions of unprocessed fly ash (0, 10, 20 and 30%) as cement replacement. The results showed that the concentrations of detected heavy metals were mostly below 1 PPM. However, the results showed higher concentrations of Al, with a greatest recorded concentration of 4.65 PPM for the mortar mix with 30% unprocessed fly ash (M17).

Table 7.11: Heavy metals concentration of mortar specimens with different unprocessed fly ash content and a Water/Binder ratio of 0.8 (Group 5) in PPM.

Metal	Fly ash=0%			Fly ash=10%			Fly ash=20%			Fly ash=30%		
	2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Al	0.05	0.32	0.89	0.02	1.33	4.35	0.02	1.63	3.92	0.07	1.80	4.65
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.10	0.10	0.00	0.09	0.13	0.00	0.07	0.08
Se	0.00	0.00	0.00	0.20	0.20	0.20	0.16	0.16	0.16	0.08	0.08	0.08
As	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00
Mo	0.00	0.00	0.00	0.00	0.03	0.04	0.00	0.04	0.04	0.00	0.04	0.04
Cr	0.00	0.00	0.00	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Pb	0.00	0.00	0.00	0.08	0.08	0.08	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.00	0.00	0.00	0.05	0.51	0.51	0.13	0.13	0.13	0.00	0.44	0.44



A: 0% unprocessed fly ash

B: 10% unprocessed fly ash

C: 20% unprocessed fly ash

D: 30% unprocessed fly ash

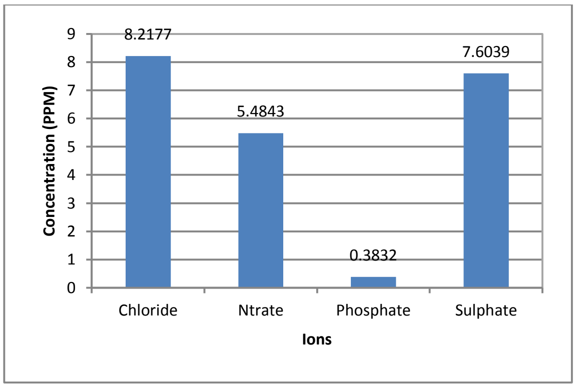
Figure 7.11: Total heavy metals concentration (28 days) of mortar specimens with different unprocessed fly ash content and Water/Binder ratio of 0.8 (Group 5) in PPM.

The Ion Chromatography System

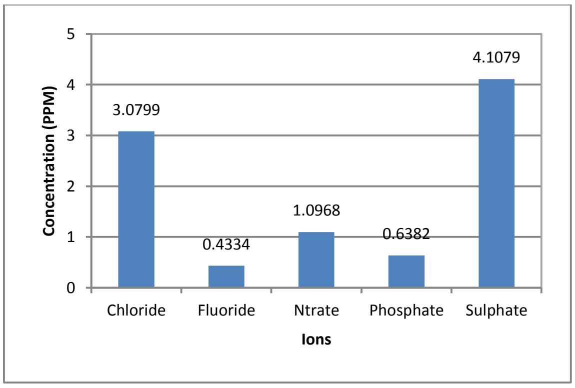
The Ion Chromatography System analysis for the control mixes is shown in Table 7.12 and Figure 7.12. The concentration of detected ions was relatively low and mostly below 1 PPM. However the results showed higher concentrations of a number of ions including Cl^- , NO_3^-, & HSO_4^-. The greatest ion concentrations were recorded as follows; 8.22 and 5.48 PPM of Cl^- and NO_3^- respectively for the mortar mix with 0% unprocessed fly ash (M14), and 14.46 PPM of HSO4- for the mix with 30% unprocessed fly ash (M17).

Table 7.12: Ion analysis of mortar specimens with different unprocessed fly ash content and a Water/Binder ratio of 0.8.

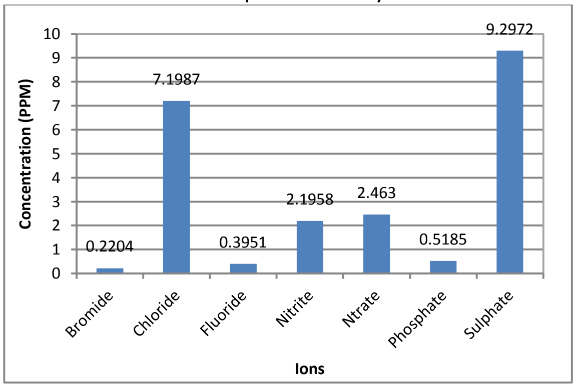
Ion	Formula	Fly ash=0%			Fly ash=10%			Fly ash=20%			Fly ash=30%		
		2H	8D	28D	2H	8D	28D	2H	8D	28D	2H	8D	28D
Bromide	Br^-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00
Chloride	Cl^-	0.79	3.57	8.22	0.63	1.94	3.08	0.71	3.19	7.20	1.95	3.43	7.36
Fluoride	F^-	0.00	0.00	0.00	0.00	0.25	0.43	0.00	0.21	0.40	0.00	0.00	0.16
Nitrite	NO_2^-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.20	0.61	0.61	0.61
Nitrate	NO_3^-	0.96	4.25	5.48	0.00	0.34	1.10	0.00	1.77	2.46	0.00	1.75	3.93
Phosphate	PO_4^{3-}	0.38	0.38	0.38	0.00	0.64	0.64	0.00	0.00	0.52	0.00	0.00	0.00
Sulphate	SO_4^{-2}	1.90	3.49	7.60	1.30	1.30	4.11	2.62	5.79	9.30	3.02	5.24	14.46



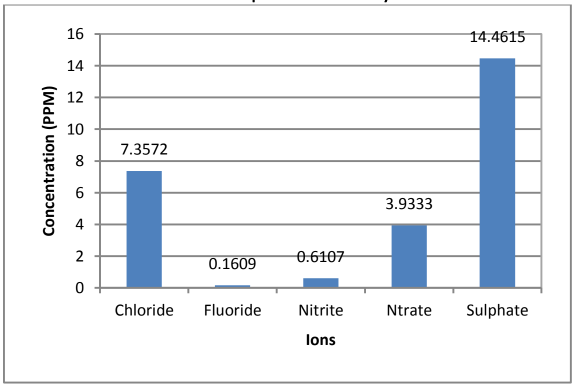
A: 0% unprocessed fly ash



B: 10% unprocessed fly ash



C: 20% unprocessed fly ash



D: 30% unprocessed fly ash

Figure 7.12: Total ions concentration (28 days) of mortar specimens with different unprocessed fly ash content and a Water/Binder ratio of 0.8 (Group 5) in PPM.

7.5 CONCLUSIONS

The main conclusions of this chapter are as follows;

- The use of both RSS and unprocessed fly ash in cement-based systems showed no signs of significant pollution to the surrounding water.
- Safe levels of heavy metals and ions were detected in the leachant (the water in direct contact with the test specimens).
- The quality of the leachant (the water in direct contact with the test specimens) met the requirements of the EU Ground Water Directive.

CHAPTER 8: CORRELATION BETWEEN DIFFERENT PROPERTIES

8.1 INTRODUCTION

Compressive strength is considered to be one of the most important engineering properties that is used to assess the quality of cement-based products. It is therefore essential for engineering professionals to correctly understand the way that strength develops with time, and to evaluate the influence of other parameters including mix composition, porosity and density.

For a better understanding of how compressive strength relates with other parameters, it is essential to assess the correlation between various properties and to develop numerical functions that link them together. This can be achieved by using the most recent computational technology, which enables us to undertake a thorough analysis for the collected data and to develop equations that relate different properties. Such technology includes computer software such as MS Excel

Correlating the strength with more than a variable is a challenging task and it may therefore require more effort and time, as well as more understanding to the available technology. However, it is now easier for the researchers to utilise the advanced software available in the market, such as MS Excel, to spot any trend and relationship between different properties.

8.2 AIMS AND OBJECTIVES

The aim of this chapter is to investigate the correlation between different physical and mechanical properties of cement-based materials incorporating RSS and unprocessed fly ash (Series 1 and Series 3). In particular, this chapter will discuss the relationship between compressive strength and various properties including Ultrasonic Pulse Velocity (UPV), Total Water Absorption (TWA), and flexural strength. This chapter also discusses the relationship between the compressive strength with curing age and with one additional parameter including either RSS content, sand content or fly ash content.

8.3 COMPRESSIVE STRENGTH AND ULTRASONIC PULSE VELOCITY (UPV)

The relationship between the compressive strength and UPV of the mortar mixes with different RSS content (Group 1) is shown in Figure 8.1. The figure shows a clear trend in the compressive strength with UPV, and it is evident that the compressive strength increased when the UPV values also increased at all curing ages. The relationship can be expressed using an exponential curve. The correlation is relatively strong as R^2 value equals to 0.86.

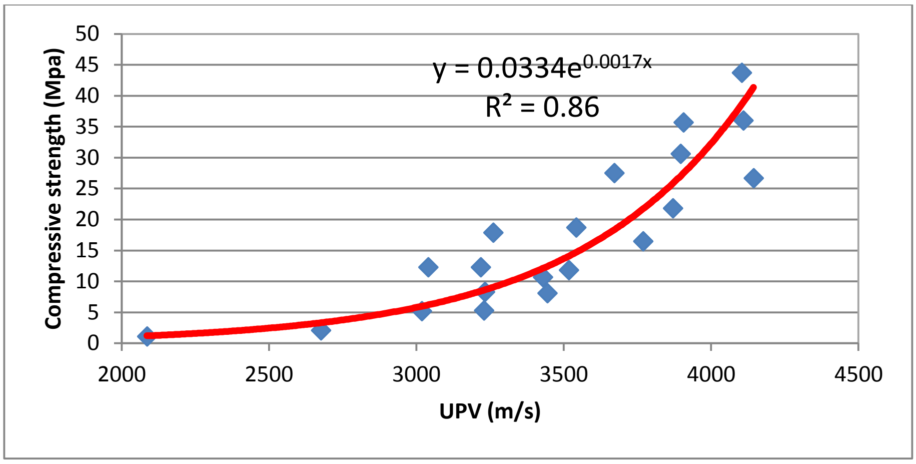


Figure 8.1: The relationship between compressive strength and UPV of mortar mixes with different RSS/Cement ratios (Group 1).

The relationship between the compressive strength and UPV of the mortar mixes with different sand content (Group 2: M5, M3, M6 and M7) is shown in Figure 8.2. The figure clearly demonstrates that the compressive strength increased with the UPV at all curing ages. The correlation is not as strong as for Group 1 and R^2 equals to 0.65.

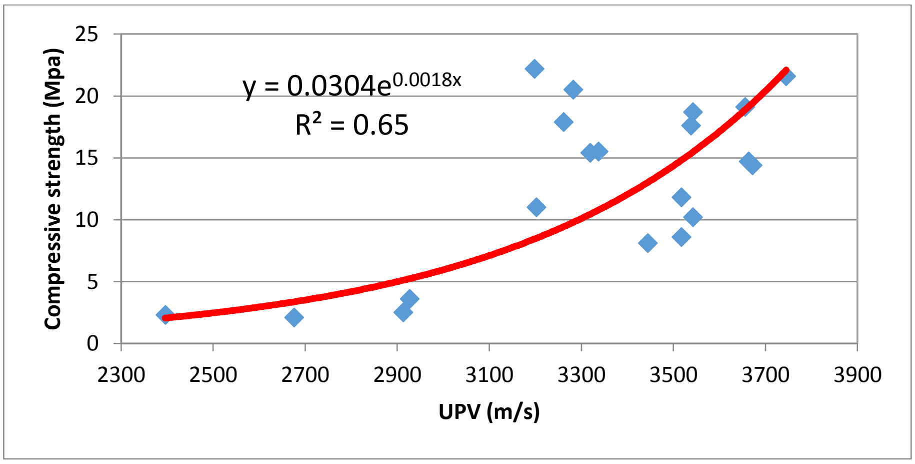


Figure 8.2: The relationship between compressive strength and UPV of mortar mixes with different sand content (Group 2).

The relationship between the compressive strength and UPV of the mortar mixes with different unprocessed fly ash content and different RSS content (Groups 3 and 4) is shown in Figure 8.3 and Figure 8.4. The results showed that the compressive strength increased with the increase of UPV for all unprocessed fly ash replacements and for both RSS/Binder ratios (0.65 and 0.8). R2 values range between 0.83-0.86.

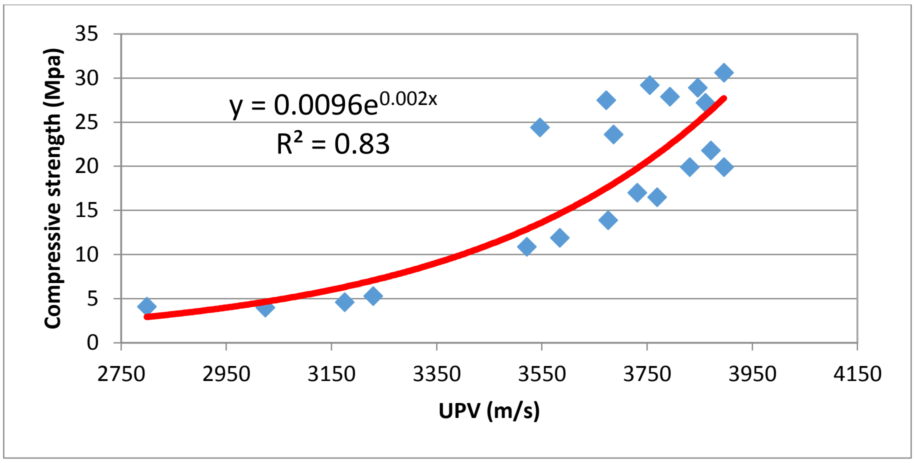


Figure 8.3: The relationship between compressive strength and UPV of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3).

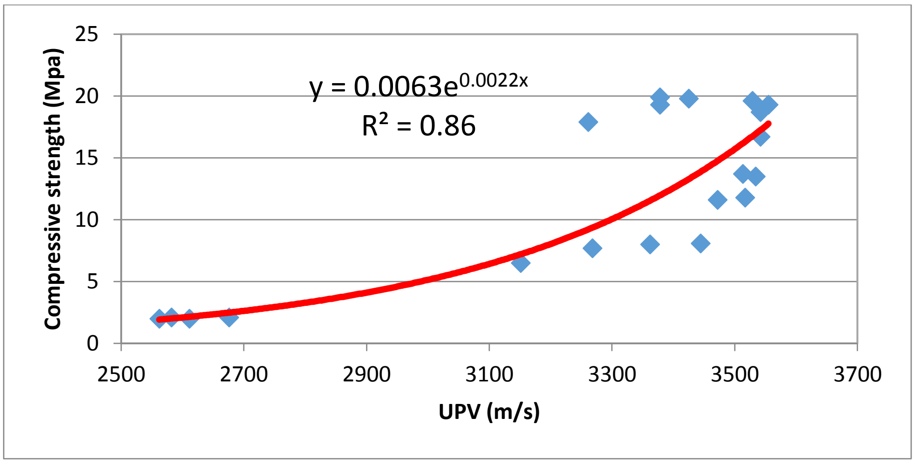


Figure 8.4: The relationship between compressive strength and UPV of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4).

For the control mixes (Group 5: M14, M15, M16 and M17), the relationship between the compressive strength and UPV is shown in Figure 8.5. The figure shows that the compressive strength increased when the UPV increased. The correlation for this group is very strong as R^2 value is 0.95.

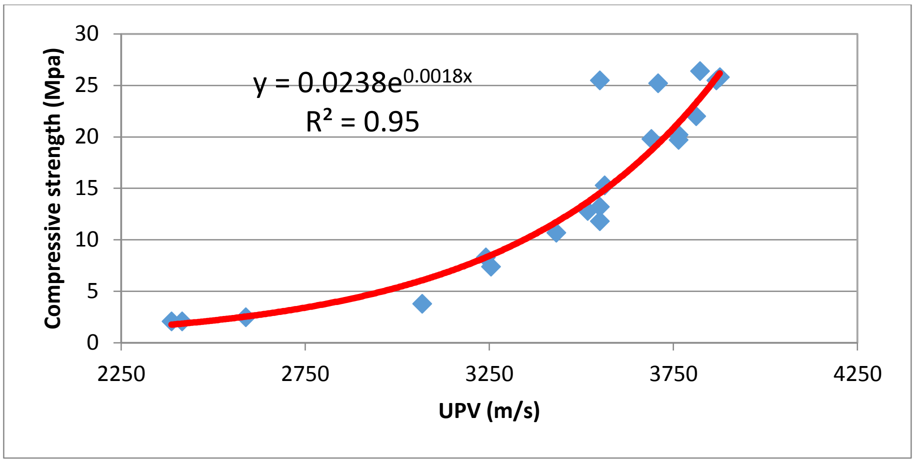


Figure 8.5: The relationship between compressive strength and UPV of the control mixes with different unprocessed fly ash content and Water/Binder ratio of 0.8 (Group 5).

For the concrete mixes (Series 3), the relationship between the compressive strength and UPV is presented in Figure 8.6. The figure clearly shows that the compressive strength increased when the UPV increased. The correlation is relatively strong and R^2 value equals to 0.89.

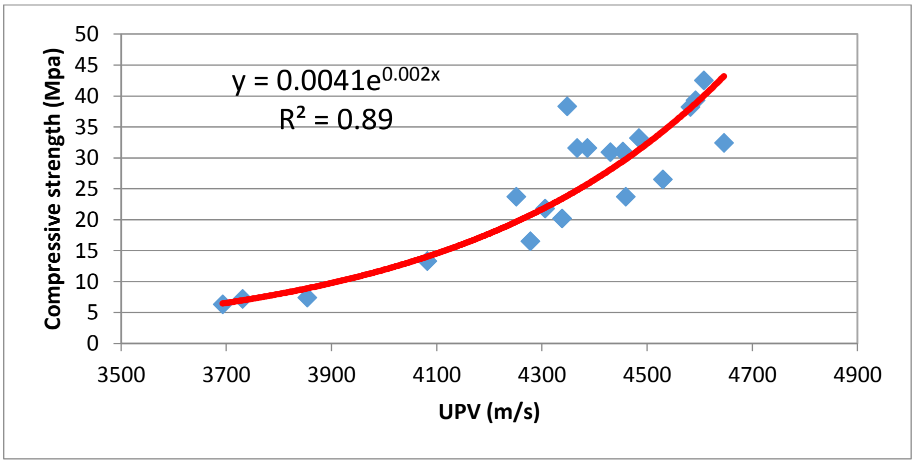


Figure 8.6: The relationship between compressive strength and UPV of the concrete mixes (Series 3).

8.4 COMPRESSIVE STRENGTH AND TOTAL WATER ABSORPTION (TWA)

The relationship between the compressive strength and TWA of mortar mixes with different RSS content (Group 1: M1, M2, M3 and M4) is shown in Figure 8.7. The figure shows a clear trend in compressive strength with TWA, and it is evident that the compressive strength increased when the TWA decreased. The correlation is not very strong and R^2 value is 0.55.

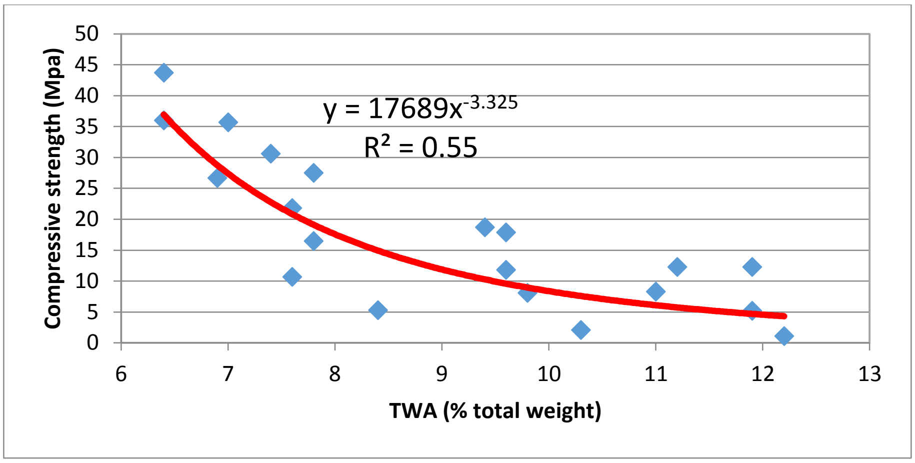


Figure 8.7: The relationship between compressive strength and TWA of mortar mixes with different RSS/Cement ratios (Group 1).

For the mortar mixes with different sand content (Group 2: M5, M3, M6 and M7), the relationship between the compressive strength and TWA is shown in Figure 8.8. The figure shows a strong correlation and presented that compressive strength increased when TWA decreased. However, the correlation is not strong and R^2 value equals to 0.03.

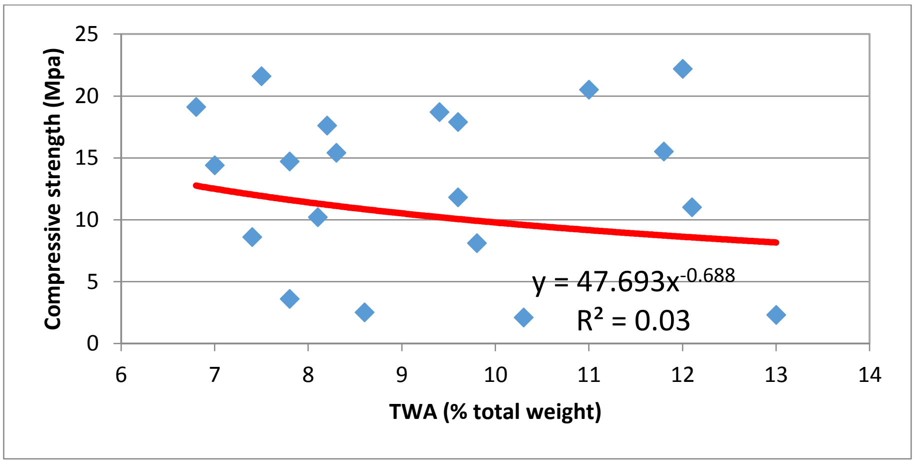


Figure 8.8: The relationship between compressive strength and TWA of mortar mixes with different sand content (Group 2).

For the mortar mixes with different unprocessed fly ash content and different RSS content (Groups 3 and 4), the relationship between the compressive strength and TWA is presented in Figure 8.9 and Figure 8.10. Both figures demonstrate that the compressive strength increased when the TWA decreased for both RSS RSS/Binder ratios (0.65 and 0.8). R^2 values range between 0.28-0.29.

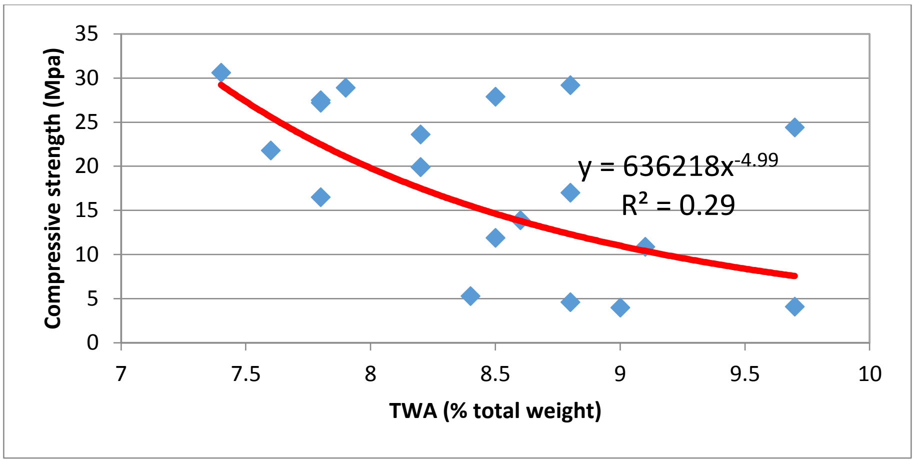


Figure 8.9: The relationship between compressive strength and TWA of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3)

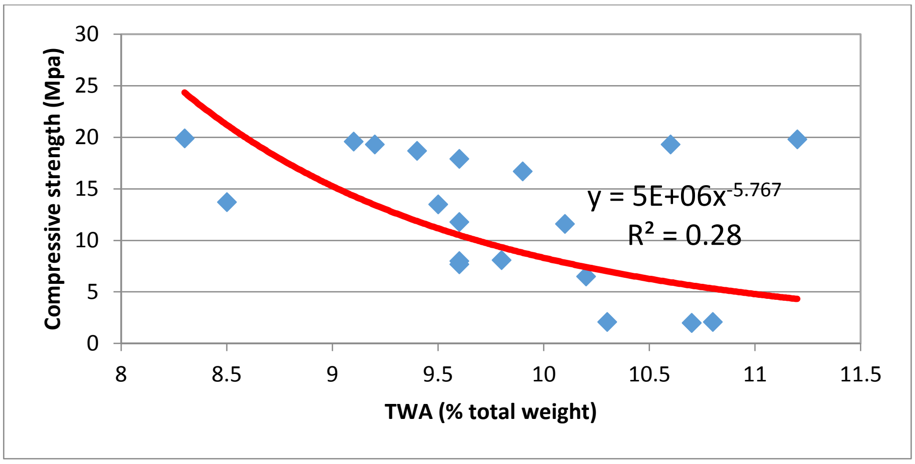


Figure 8.10: The relationship between compressive strength and TWA of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4).

For the control mixes (Group 5), the relationship between the compressive strength and TWA is presented in Figure 8.11. The figure shows that the compressive strength generally correlates negatively with TWA, as the compressive strength increased when TWA decreased. The correlation is not very strong and R^2 value is 0.27.

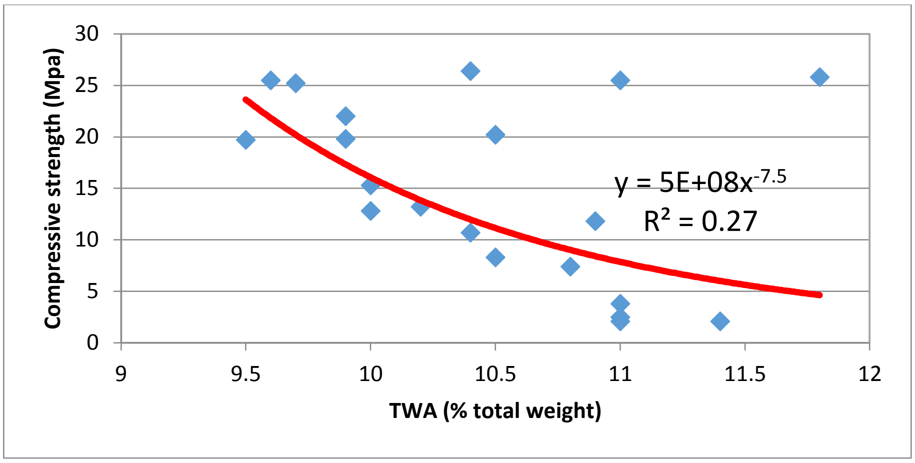


Figure 8.11: The relationship between compressive strength and TWA of the control mixes with different unprocessed fly ash content and Water/Binder ratio of 0.8 (Group 5).

For the concrete mixes (Series 3), the relationship between compressive strength and TWA is shown in Figure 8.12. The figure clearly shows that the compressive strength increased when the TWA decreased. R2 for this relationship is 0.39.

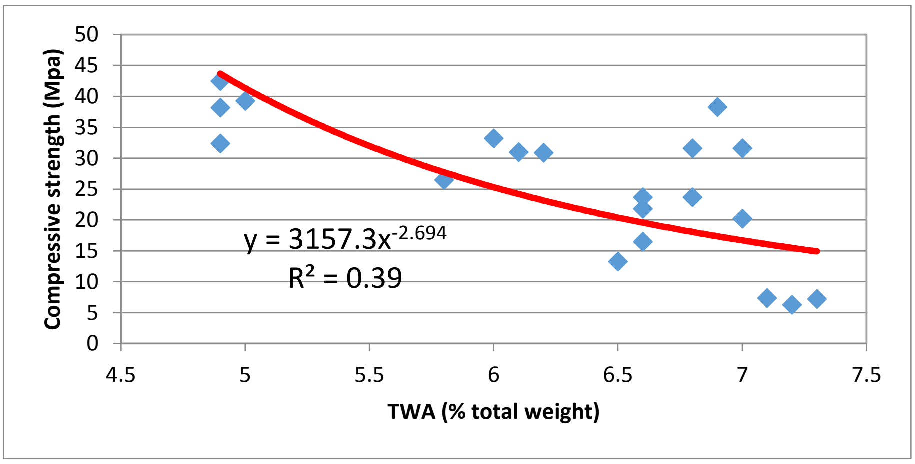


Figure 8.12: The relationship between compressive strength and TWA of the concrete mixes (Series 3).

8.5 FLEXURAL STRENGTH AND COMPRESSIVE STRENGTH

The relationship between the flexural strength and compressive strength of the mortar mixes with different RSS content (Group 1: M1, M2, M3 and M4) is shown in Figure 8.13. The figure indicates that flexural strength strongly correlated with the compressive strength, as the flexural strength increased when the compressive strength increased. The correlation is relatively strong and R^2 value equals to 0.77.

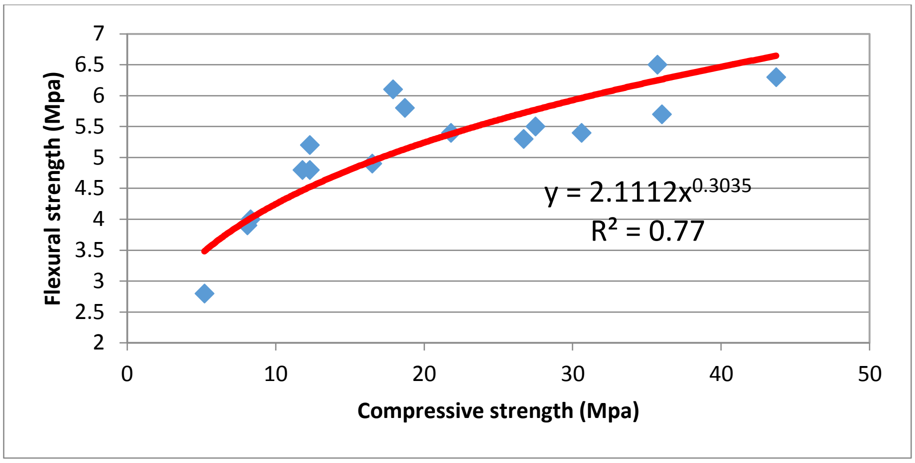


Figure 8.13: The relationship between flexural strength and compressive strength of mortar mixes with different RSS/Cement ratios (Group 1).

For the mortar mixes with different unprocessed fly ash content and different RSS/Binder ratios (Groups 3 and 4), the relationship between the flexural strength and compressive strength is shown in Figure 8.14 and Figure 8.15. The results showed that the flexural strength increased with increasing the compressive strength for all unprocessed fly ash content and for both RSS/Binder ratios. R2 values range between 0.83-0.84.

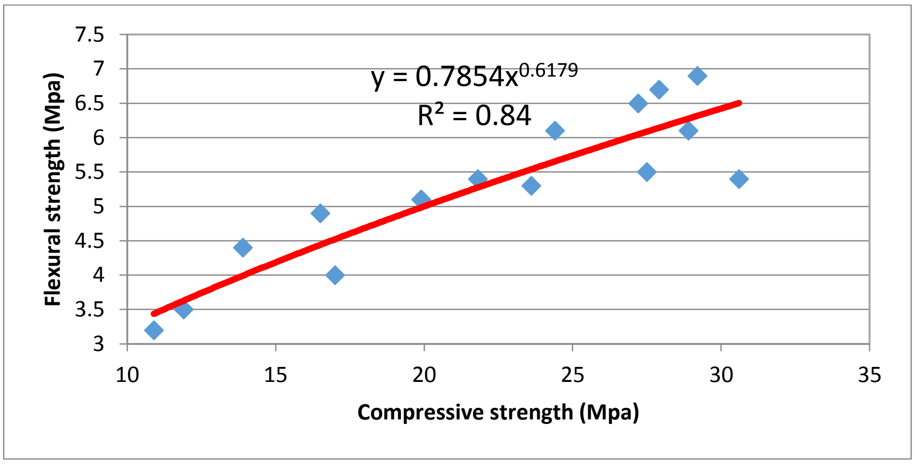


Figure 8.14: The relationship between flexural strength and compressive strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3).

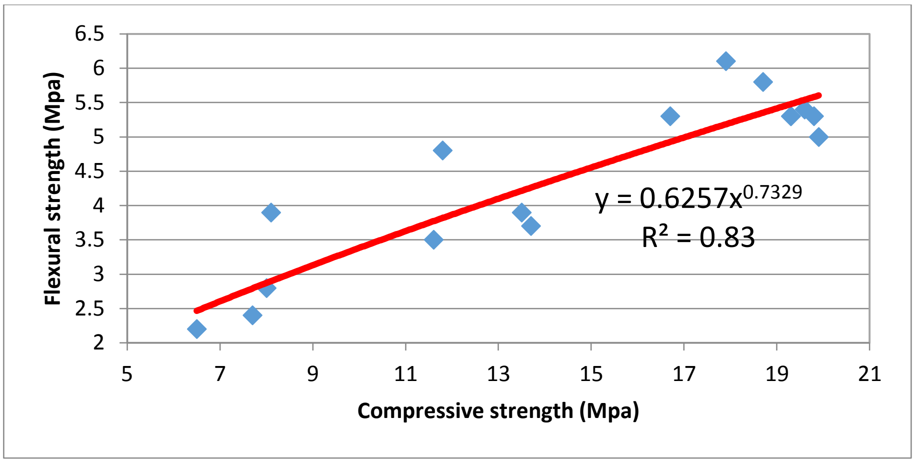


Figure 8.15: The relationship between flexural strength and compressive strength of mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Group 4).

For the control mixes (Group 5: M14, M15, M16 and M17), the relationship between the flexural strength and compressive strength is shown in Figure 8.16. The figure demonstrates a positive relationship, as the flexural strength increased when the compressive strength increased, and R^2 value is 0.71.

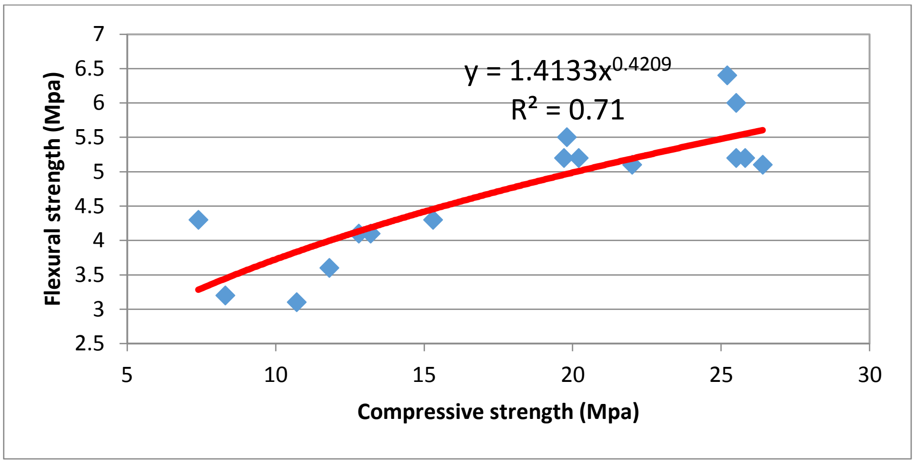


Figure 8.16: The relationship between flexural strength and compressive strength of the control mixes with different unprocessed fly ash content and Water/Binder ratio of 0.8 (Group 5).

The relationship between the flexural strength and compressive strength of the concrete mixes (Series 3) is shown in Figure 8.17. The figure indicates that the flexural strength increased when the compressive strength increased. The correlation is relatively strong and R^2 value equals to 0.74.

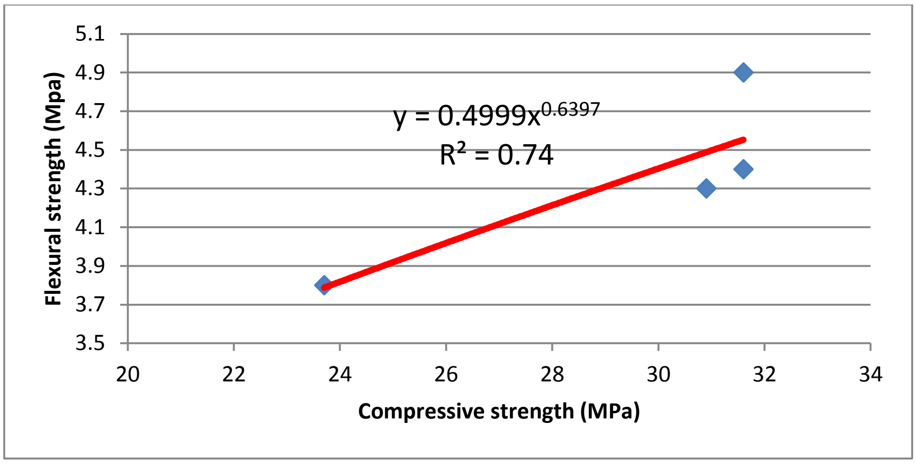


Figure 8.17: The relationship between flexural strength and compressive strength of the concrete mixes (28 days curing age only).

Further correlations were evaluated and no substantial findings were determined. More details are available in Figures ApxC.1, ApxC.2, ApxC.3, ApxC.4, ApxC.5 and ApxC.6 in Appendix C.

8.6 MULTIPLE REGRESSION

Multiple regressions were applied, with the aid of Excel 2010, to model the relationships between two or more explanatory variables and a response variable by fitting a curve equation to the collected data. In this analysis, compressive strength (the response variable) was related to a number of explanatory variables including either RSS content, sand content, unprocessed fly ash content, and curing age. A number of curve equations were therefore developed as summarised below:

For the mortar mixes with different RSS content (Group 1: M1, M2, M3 and M4), the relationship between the compressive strength and curing age is presented in Figure 8.18. The figure also includes a logarithmic fitted curve that best related the compressive strength with curing age. A generic function can be therefore derived and as presented in Equation 8.1. Table 8.1 lists the equation coefficients (μ_1 and λ_1) for each RSS content.

$$f_c' = \mu_1 * \ln(CA) + \lambda_1 \qquad Equation\ 8.1$$

Where f_c' is compressive strength in MPa, CA is curing age in days, and μ_1 and λ_1 are equation coefficients.

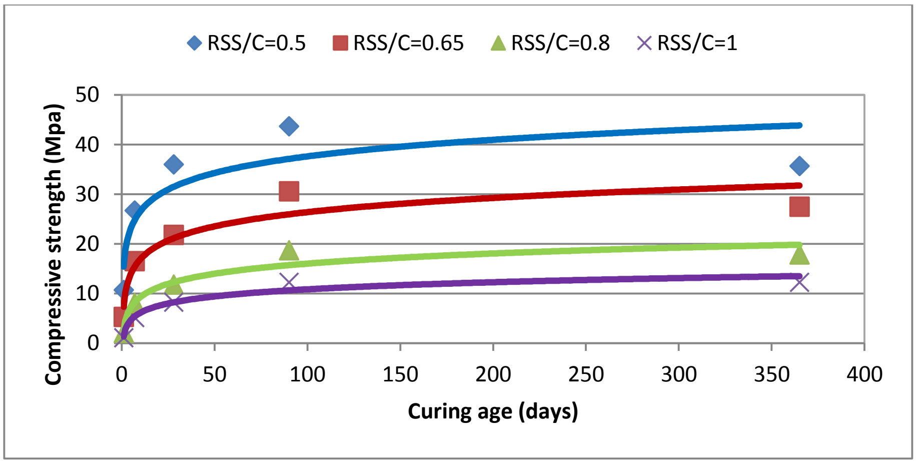


Figure 8.18: Relationship between compressive strength with curing age for mortar mixes with different RSS content (experimental and fitted)

Table 8.1: Coefficients for Equations 8.1.

RSS/Cement	$f'_c = \mu_1 * \ln(CA) + \lambda_1$		
	μ_1	λ_1	R^2
0.5	4.81	15.45	0.76
0.65	4.13	7.40	0.89
0.8	2.94	2.51	0.93
1	2.06	1.39	0.95

The relationship of μ_1 and λ_1 with RSS/Cement ratio is demonstrated in Figure 8.19. The figure also shows the best fit curve with the corresponding equation for each coefficient.

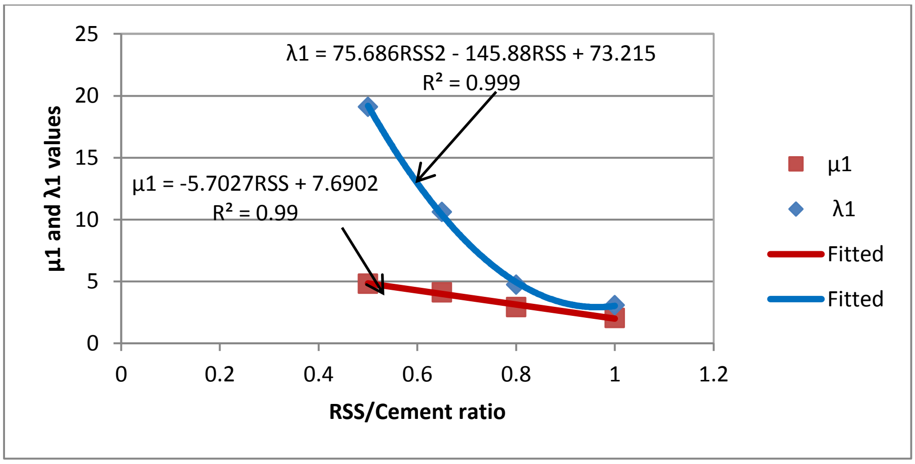


Figure 8.19: Relationship between µ1 and λ1 with RSS/Cement ratio (Equation 8.1).

By replacing μ_1 and λ_1 coefficients with their corresponding functions shown in Figure 8.19, Equation 8.1 can be rewritten to include the effect of varying RSS content on compressive strength. The amended relationship is presented in Equation 8.1a.

$$f_c' = (-5.7027 * RSS + 7.6902) * \ln(CA) + (75.686 * RSS^2 - 154.88 * RSS + 73.215) \qquad Equation\ 8.1a$$

By re-arranging the Equation, we get

$$f_c' = 75.686 * RSS^2 - (154.88 + 5.7027 * \ln(CA)) * RSS + (7.6902 * ln(age) + 73.215) \quad Equation\ 8.1b$$

Where RSS is RSS/Cement ratio.

The relationship between the experimental and predicted compressive strength is presented in Figure 8.20. More details are available in Figure ApxC.7 in Appendix C.

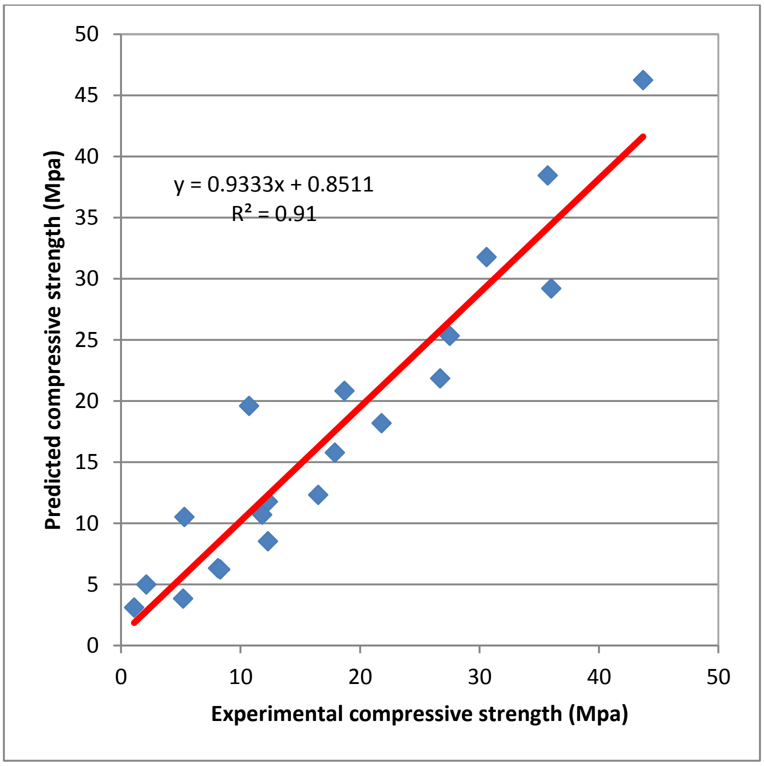


Figure 8.20: Experimental and predicted compressive strength for mortar mixes with different RSS/Cement ratios (Equation 8.1b).

For the mortar mixes with different sand content (Group 2: M5, M3, M7 and M7), the relationship between the compressive strength and curing age is presented in Figure 8.21. A general relationship was developed using a logarithmic curve and is presented in Equation 8.2. Table 8.2 lists the equation coefficients (μ_2 and λ_2), and Figure 8.22 shows how they correlate with the sand content. Figure 8.22 also includes the best fit curves, with their corresponding functions that relate μ_2 and λ_2 coefficients with the sand content.

$$f_c' = \mu_2 * \ln(CA) + \lambda_2 \qquad Equation\ 8.2$$

Where f_c' is compressive strength in Mpa, CA is curing age in days, and μ_2 & λ_2 are the equation coefficients.

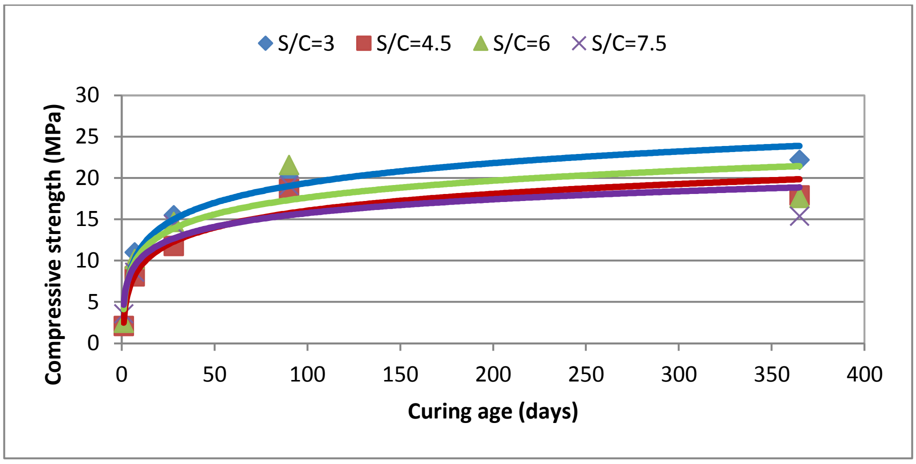


Figure 8.21: Relationship between compressive strength with curing age for mortar mixes with different sand content (experimental and fitted).

Table 8.2: Coefficients for Equations 8.2.

Sand to cement ratio	$f_c' = \mu_2 * \ln(CA) + \lambda_2$		
	μ_2	λ_2	R^2
3	3.47	3.43	0.97
4.5	2.94	2.51	0.93
6	2.94	4.11	0.83
7.5	2.40	4.69	0.80

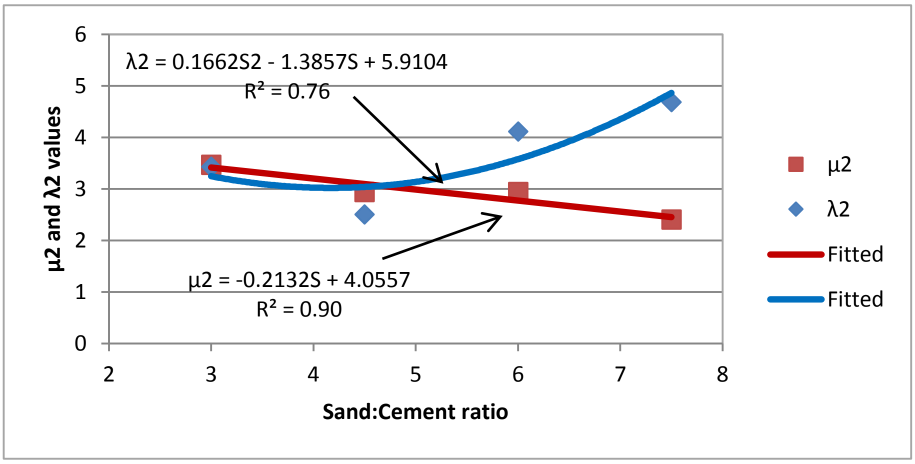


Figure 8.22: Relationship between μ_2 and λ_2 with the sand to cement ratio (Equation 8.2).

By replacing μ_2 and λ_2 coefficients with their corresponding formulas shown in Figure 8.22, to include the influence of varying sand content on the compressive strength, we get

$$f_c' = (-0.2132 * S + 4.0557) * \ln(CA) + (0.1662 * S^2 - 1.3857 * S + 5.9104) \qquad \textit{Equation } 8.2a$$

By re-arranging Equation 8.2a, we get

$$f_c' = (0.1662) * S^2 + (1.3857 - 0.2132 * \ln(CA)) * S + (04.0557 * \ln(CA) + 5.9104) \qquad \textit{Equation } 8.2b$$

Where S is sand to cement ratio.

The relationship between the experimental and predicted compressive strength for this group of mixes is shown in Figure 8.23. More details are available in Figure ApxC.8 in Appendix C.

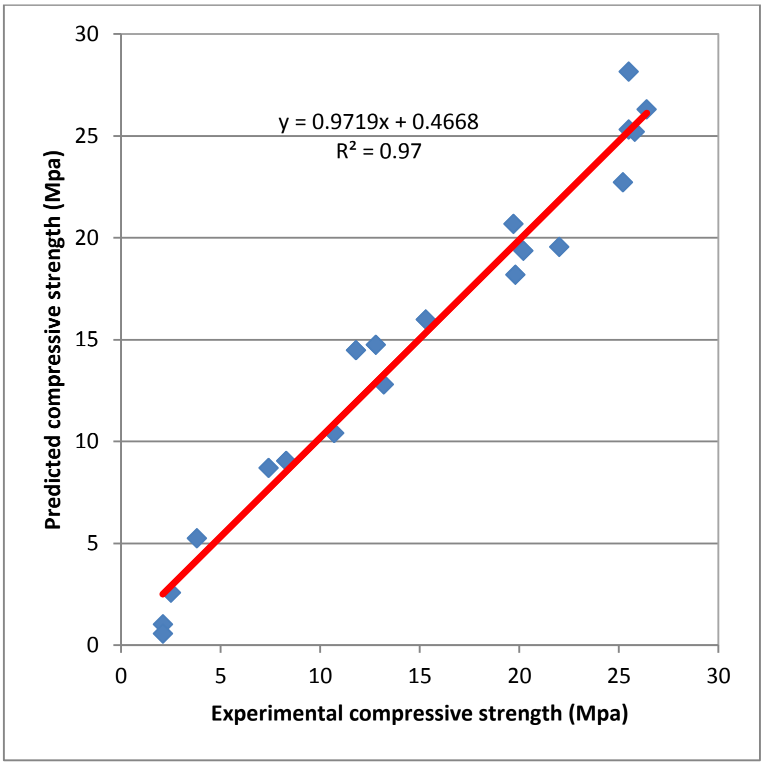


Figure 8.23: the relationship between the experimental and predicted compressive strength for mortar mixes with different Sand content (Equation 8.2b).

For the mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (Group 3: M2, M11, M12 and M13), the relationship between the compressive strength and curing age is shown in Figure 8.24. The relationship can be expressed using Equation 8.3, which was derived from the best fit curves shown in Figure 8.24. Table 8.3 lists the equation coefficients (μ_3 and λ_3), and Figure 8.25 presents how they correlate with the content of unprocessed fly ash.

$$f_c' = \mu_3 * \ln(CA) + \lambda_3 \qquad Equation\ 8.3$$

Where f_c' is compressive strength in MPa, CA is curing age in days, and μ_3 & λ_3 are equation coefficients.

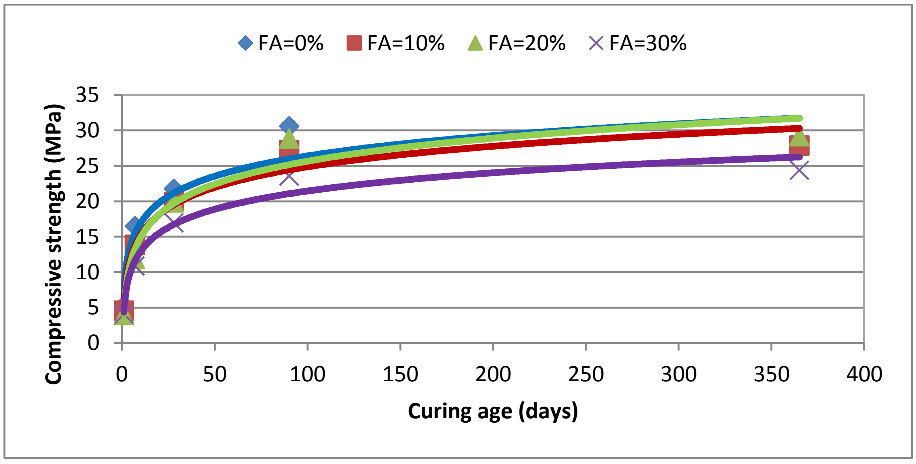


Figure 8.24: Relationship between compressive strength with curing age for mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.65 (experimental and fitted).

Table 8.3: Coefficients (μ_3 & λ_3) for Equation 8.3.

Fly ash %	$f_c' = \mu_3 * \ln(CA) + \lambda_3$		
	μ_3	λ_3	R^2
0	4.13	7.40	0.89
10	4.19	5.55	0.96
20	4.68	4.10	0.95
30	3.71	4.36	0.96

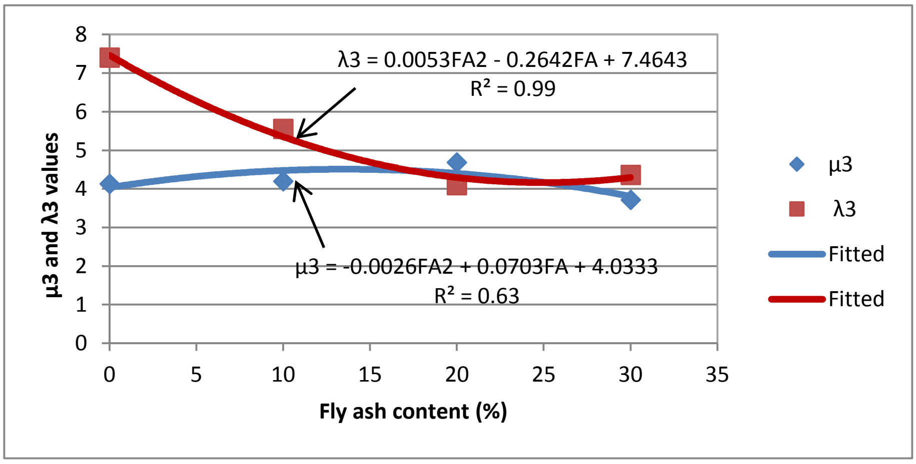


Figure 8.25: Relationship of μ_3 and λ_3 with unprocessed fly ash content (Equation 8.3).

By replacing μ_3 and λ_3 in Equation 8.3 with the best fit curves shown in Figure 8.25, to include the effect of varying unprocessed fly ash content on compressive strength, we get

$$f'c = (-0.0026 * FA^2 + 0.0703 * FA + 4.0333) * \ ln(CA) + 0.0053 * FA^2 - 02642 * FA + 7.4643 \qquad Equation\ 8.3a$$

By re-arranging Equation 8.3a, we get

$$f'c = \left(0.0053 - 0.0026 * lin(CA)\right) * FA^2 + (0.0703 * \ln(CA) - 0.2642) * FA + (4.033 * \ln(CA) + 7.4643) \qquad Equation\ 8.3b$$

Where FA is % unprocessed fly ash content.

The relationship between the experimental and predicted compressive strength for this group of mixes is shown in Figure 8.26. More details are available in Figure ApxC.9 in Appendix C.

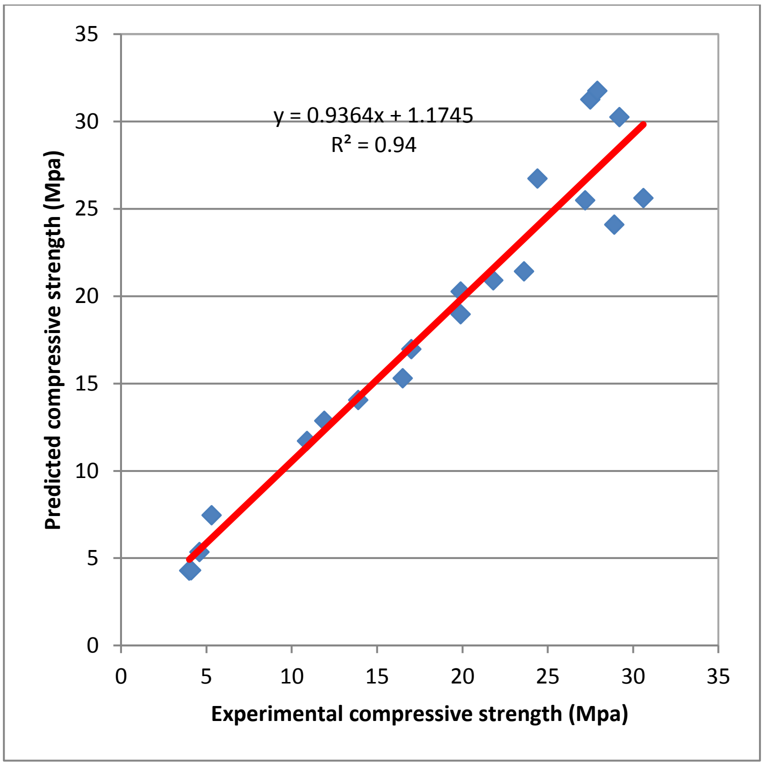


Figure 8.26: Experimental and predicted compressive strength for mortar mixes with different unprocessed fly ash content and RSS/Binder ratios of 0.65(Equation 8.3b)

For the mortar mixes with unprocessed fly ash and RSS/Binder ratio of 0.8 (Group 4: M3, M8, M9 and M10), the relationship between the compressive strength and curing age is shown in Figure 8.27. The figure also shows the best fit curves that relate the compressive strength with curing age for each unprocessed fly ash content. A generic equation was therefore developed and as presented in Equation 8.4. Table 8.4 lists the coefficients (µ4 and λ4), and Figure 8.28 shows how they correlate with unprocessed fly ash content.

$$f_c' = \mu_4 * \ln(CA) + \lambda_4 \qquad Equation\ 8.4$$

Where f_c' is compressive strength in MPa, CA is curing age in days, and μ_4 & λ_4 are equation coefficients.

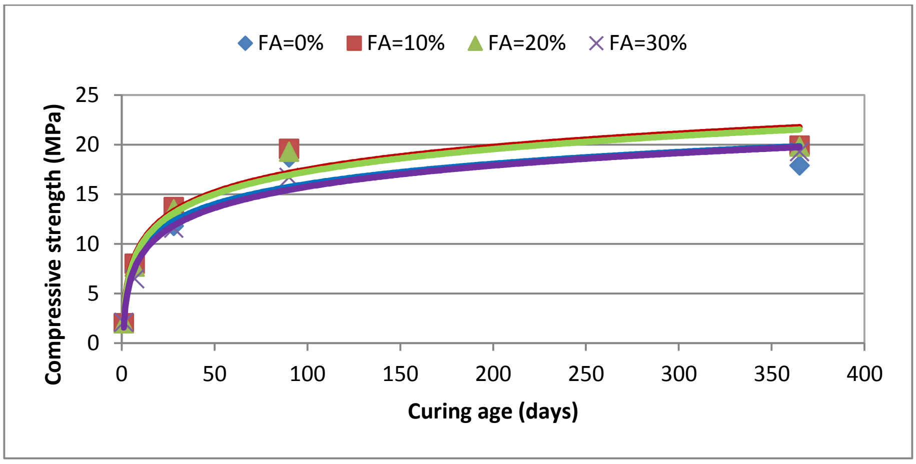


Figure 8.27: Relationship between compressive strength and curing age for mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (experimental and fitted).

Table 8.4: Coefficients (μ_4 and λ_4) for Equation 8.4.

Fly ash %	$f_c' = \mu_4 * \ln(CA) + \lambda_4$		
	μ_4	λ_4	R^2
0	2.94	2.51	0.93
10	3.30	2.28	0.96
20	3.29	2.16	0.96
30	3.08	1.57	0.98

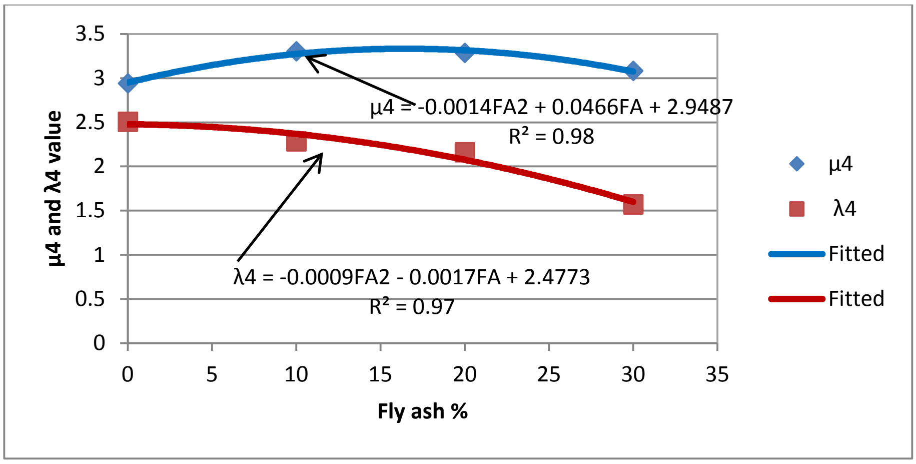


Figure 8.28: Relationship of μ_4 and λ_4 with unprocessed fly ash content (Equation 8.4).

By replacing μ_4 and λ_4 in Equation 8.4 with the best fit curve shown in Figure 8.28, to include the effect of varying unprocessed fly ash content on compressive strength, we get

$$f'c = (-0.0014 * FA^2 - 0.0466 * FA + 2.9487) * \ ln(CA) + 0.0009 * FA^2 - 0.0017 * FA + 2.4773 \qquad Equation\ 8.4a$$

By re-arranging Equation 8.4a, we get

$$f'c = \left(0.0009 - 0.0014 * lin(CA)\right) * FA^2 + (0.0466 * \ln(CA) - 0.0017) * FA + (2.9487 * \ln(CA) + 2.4773) \qquad Equation\ 8.4b$$

Where FA is % unprocessed fly ash content.

The relationship between the experimental and predicted compressive strength for this group of mixes is shown in Figure 8.29. More details are available in Figure ApxC.10 in Appendix C.

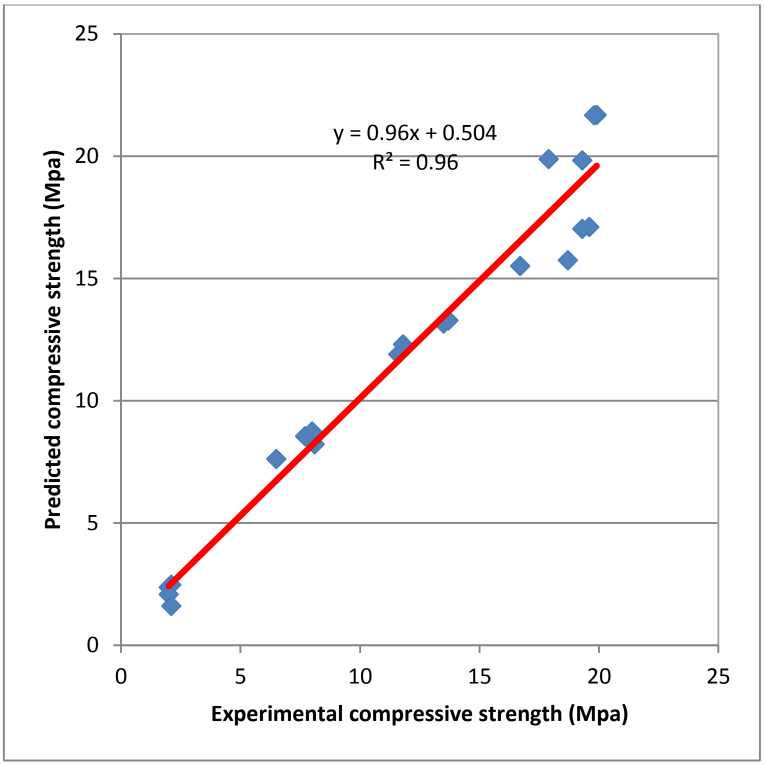


Figure 8.29: The relationship between the experimental and predicted compressive strength for the mortar mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.8 (Equation 8.4b).

For the control mixes (Group 5: M14, M15, M16 and M17), the relationship between compressive strength and curing age is shown in Figure 8.30. The figure also includes the best fit curves for each unprocessed fly ash content. A generic equation was therefore developed and as presented in Equation 8.5 with the coefficients (μ_5 and λ_5) listed in Table 8.5.

$$f_c' = \mu_5 * \ln(CA) + \lambda_5 \qquad \textit{Equation } 8.5$$

Where f_c' is compressive strength in MPa, CA is curing age in days, and μ_5 & λ_5 are equation coefficients.

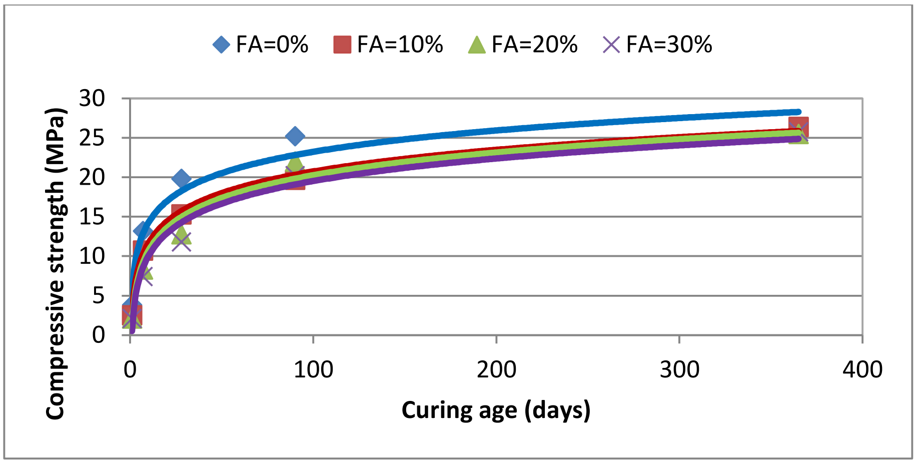


Figure 8.30: Relationship between compressive strength and curing age for control mixes with different unprocessed fly ash content and Water/Binder ratio of 0.8 (experimental and fitted).

Table 8.5: Coefficients (μ_5 and λ_5) for Equation 8.5.

Fly ash %	$f'_c = \mu_5 * \ln(CA) + \lambda_5$		
	μ_5	λ_5	R^2
0	3.90	5.26	0.95
10	3.96	2.51	0.997
20	4.16	1.08	0.997
30	4.13	0.51	0.97

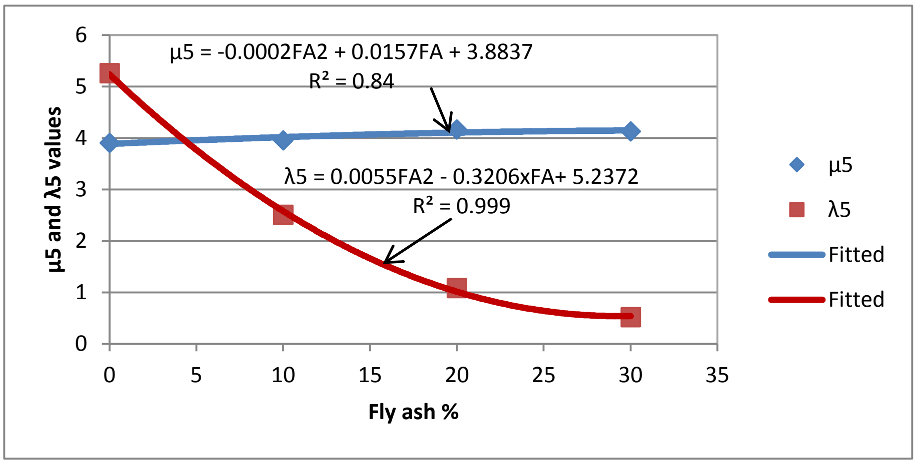


Figure 8.31: Relationship of μ_5 and λ_5 with unprocessed fly ash content (Equation 8.5).

By replacing μ_5 and λ_5 in Equation 8.5 with their corresponding best fit functions shown in Figure 8.31, to include the effect of varying unprocessed fly ash content on compressive strength, we get

$$f'c = (-0.0002 * FA^2 + 0.0157 * FA + 3.8837) * \ ln(CA) + 0.0055 * FA^2 - 0.3206 * FA + 5.23722 \qquad Equation\ 8.5a$$

By re-arranging Equation 8.5a, we get

$$f'c = \left(0.0055 - 0.0002 * lin(CA)\right) * FA^2 + (0.0157 * \ln(CA) - 0.3206) * FA + (3.8837 * \ln(CA) + 5.2372) \qquad Equation\ 8.5b$$

Where FA is % unprocessed fly ash content.

The relationship between the experimental and predicted compressive strength for this group of mixes is shown in Figure 8.32. More details are available in Figure ApxC.11 in Appendix C.

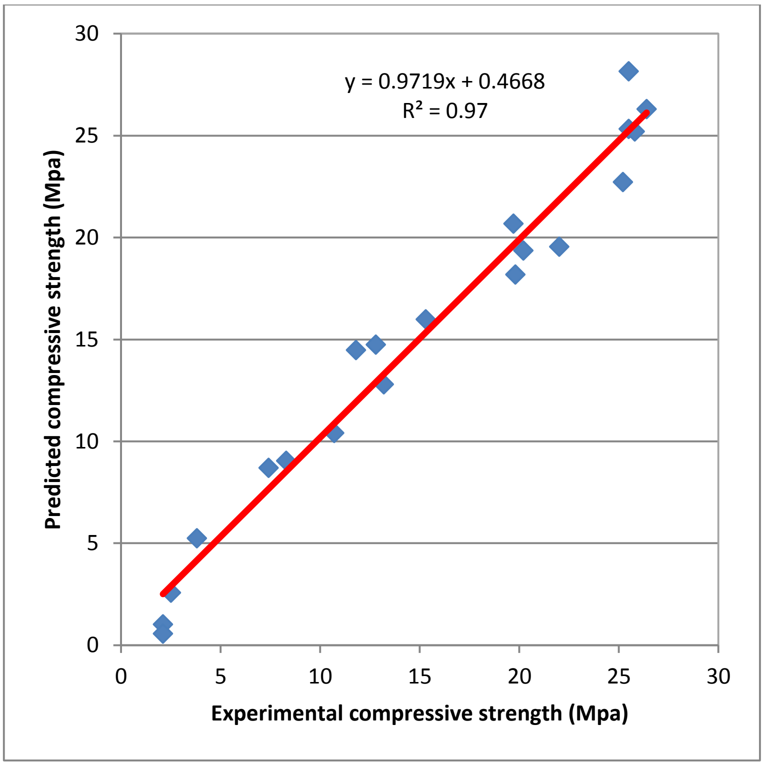


Figure 8.32: Experimental and predicted compressive strength for the control mixes with different unprocessed fly ash content and Water/Binder ratio of 0.8 (Equation 8.5b).

For the concrete mixes with different unprocessed fly ash and RSS/Binder ratio of 0.5 (Series 3), the relationship between the compressive strength and curing age is shown in Figure 8.33. The figure also shows the best fit curves for each unprocessed fly ash content. A generic equation was developed to relate compressive strength with curing age and is presented in Equation 8.6. Table 8.6 lists the coefficients (μ_6 and λ_6) for Equation 8.6.

$$f_c' = \mu_6 * \ln(CA) + \lambda_6 \qquad Equation\ 8.6$$

Where f_c' is compressive strength in MPa, CA is curing age in days, and μ_6 & λ_6 are equation coefficients.

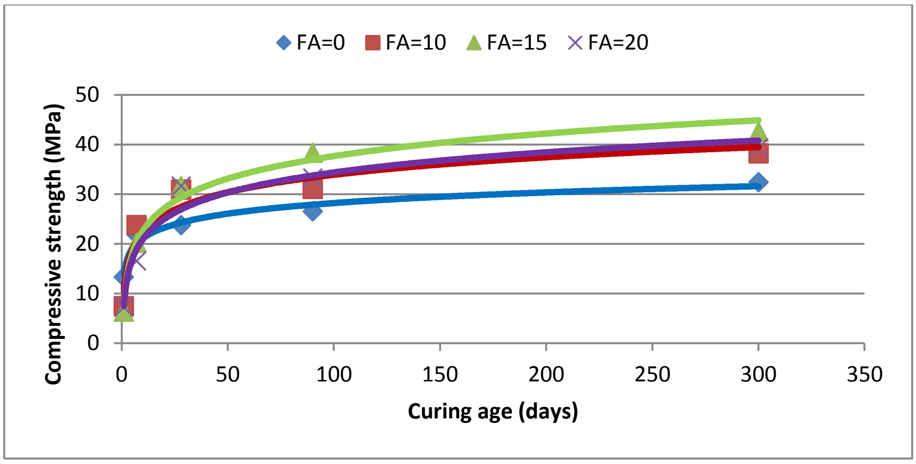


Figure 8.33: Relationship between compressive strength and curing age for the concrete mixes (experimental and fitted).

Table 8.6: Coefficients (μ_6 and λ_6) for Equation 8.6.

Fly ash %	$f_c' = \mu_6 * \ln(CA) + \lambda_6$		
	μ_6	λ_6	R^2
0	3.09	23.97	0.97
10	5.08	10.52	0.93
15	6.55	7.50	0.98
20	5.84	7.48	0.96

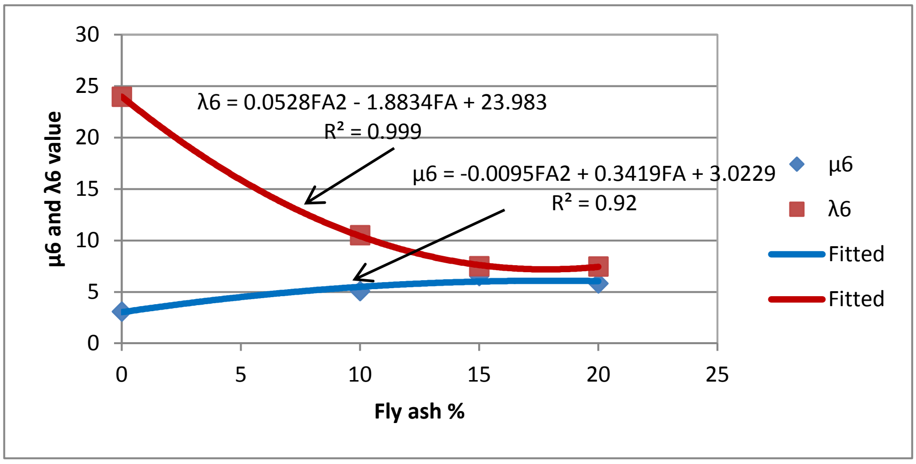


Figure 8.34: Relationship of μ_6 and λ_6 with unprocessed fly ash content (Equation 8.6).

By replacing μ_6 and λ_6 in Equation 8.6 with their corresponding best fit functions shown in Figure 8.34, to include the effect of varying unprocessed fly ash content on compressive strength, we get

$$f'c = (-0.0095 * FA^2 + 0.3419 * FA + 3.0229) * \ ln(CA) + 0.0528 * FA^2 - 1.8834 * FA + 23.983 \qquad Equation\ 8.6a$$

By re-arranging Equation 8.6a, we get

$$f'c = \left(0.0528 - 0.0095 * lin(CA)\right) * FA^2 + (0.3419 * \ln(CA) - 1.8834) * FA + (3.0229 * \ln(CA) + 23.983) \qquad Equation\ 8.6b$$

Where FA is % unprocessed fly ash content.

The relationship between the experimental and predicted compressive strength for this group of mixes is shown in Figure 8.35. More details are available in Figure ApxC.12 in Appendix C.

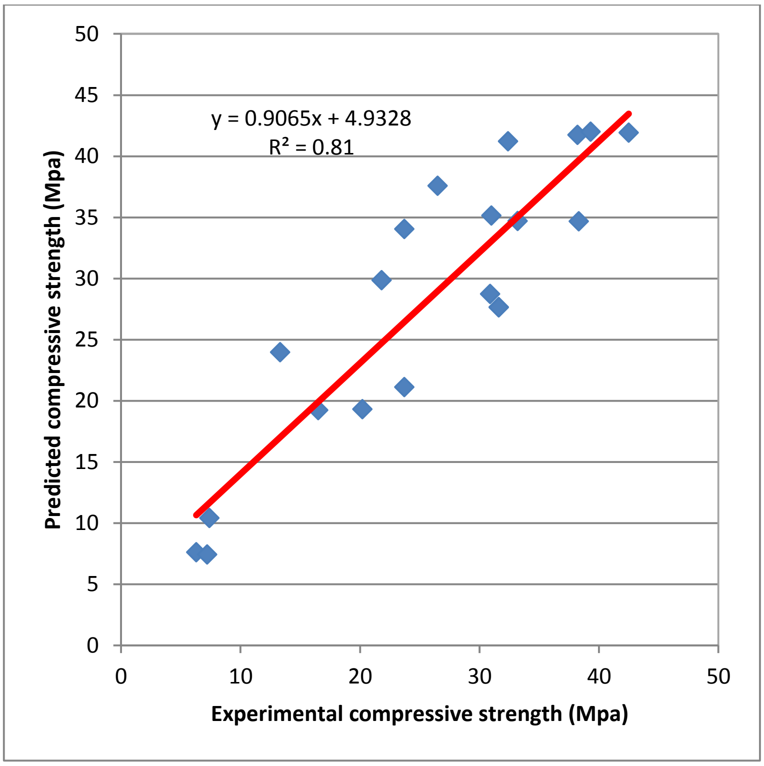


Figure 8.35: Experimental and predicted compressive strength for concrete mixes with different unprocessed fly ash content and RSS/Binder ratio of 0.5 (Equation 8.6b).

8.7 CONCLUSIONS

The main conclusion of this chapter can be summarised and as follows:

- The compressive strength positively correlated with the UPV for all mixes, as the strength increased with increasing UPV. An exponential function was suggested to express the relationship between the compressive strength and UPV
- The compressive strength correlated negatively with the TWA for all mixes. A power function was used to demonstrate the correlation between the compressive strength and TWA.
- The flexural strength correlate positively with compressive strength and the results confirmed that flexural strength increased when the compressive strength also increased. A power function was used to express the correlation between the two properties.
- Multiple regression was applied to develop functions that correlate the compressive strength with curing age and with one additional parameter. Additional parameters included RSS content, sand content, unprocessed fly ash content and water content (for the control mixes). The results showed that the predicted compressive strength values were considerably close to the experimental ones.

CHAPTER 9: DISCUSSIONS

9.1 AIMS AND OBJECTIVES

The aim of this chapter is to discuss the results of tested properties and their correlation that were reported in Chapters 4, 5, 6, 7 and 8. The tested properties include fresh & physical properties, mechanical properties, sulphate resistance (sulphate attack), and environmental properties (leaching test).

9.2 FRESH AND PHYSICAL PROPOERTIES

9.2.1 Flowability/Workability

For this experimental work, the flowability of mortar mixes that incorporated RSS increased when the content of RSS increased, and the greatest flowability value of 233mm was recorded for the mortar mix with RSS/Cement ratio of 1 (M4). Workability of cement-based systems is much dependant on a number of interacting factors including water content, aggregate/cement ratio, aggregate type and grading, fineness and shape of aggregate, porosity and absorption of aggregate, and fineness of cement. Water content is the main factor that significantly influences workability, as the addition of water increases the interparticle lubrication (Mindess et al., 2003; Neville and Brooks, 2004). This agreed with the outcome of previous research (Nematzadeh and Naghipour, 2012). The results also showed that the flowability of mortar mix that incorporated drinking water (M14) was comparatively higher than that made of RSS (M3), as the flowability value for M14 was 195mm and for M3 was 178mm. For Series 2 and 3, the flowability/workability decreased when water was replaced by RSS. This may be due to the impact of the irregularity of the suspended organics that were presented in the RSS.

The flowability of the mortar mixes that contained RSS and different sand to cement ratios increased when the sand content reduced and the greatest flowability value of 230mm was recorded for the mortar mix with sand to cement ratio of 3 (M5). This came in line with results reported elsewhere (Fernandes et al., 2007)

The addition of unprocessed fly ash into both mortar and concrete mixes significantly influenced the flowability/workability. The flowability of the mortar mixes decreased when the content of unprocessed fly ash increased, and the lowest flowability value of 107mm was recorder M13 (30% unprocessed fly ash replacement and RSS/Binder ratio of 0.65) and 113mm for M10 (30% unprocessed fly ash replacement and RSS/Binder ratio of 0.8). Additionally, the results exhibited that the reduction of RSS content significantly influenced flowability of the mortar mixes without unprocessed fly ash, but less impact was observed for mixes that contained unprocessed fly ash. The flowability of mortar mixes with drinking water (Group 5: M14, M15, M16 and M17) also decreased with the inclusion of unprocessed fly ash, and the greatest flowability value of 195mm was recorded for the mortar mix with 30% unprocessed fly ash (M14). Finally, the flowability/workability of both concrete mixes and mortar mixes with large proportion of unprocessed fly ash also decreased when the unprocessed fly ash content was included. This may be due to the presence of the coarse materials (>45µm) in the unprocessed fly ash (Figure 3.3), as workability decreases with increasing the coarse proportion in fly ash (Owens, 1979). An additional factor that influenced the workability is the Loss On Ignition (LOI) value, as it is related to the unburned carbon amount in fly ash. The porous carbon particles absorb hydration water resulting less workability (Brink and Halstead, 1956; Welsh and Burton, 1958; Minnick et al., 1971; Rehsi, 1973).

9.2.2 Density and TWA

For this experimental work, the density of mortar mixes with different RSS/Cement ratios decreased when the content of RSS increased, and the greatest density of 2249 Kg/m^3 was recorded for the mortar mix with RSS/Cement ratio of 0.5 (M1). Both density and voids content are largely dependent on water/cement ratio, compaction ratio, hydration degree, and are also dependant on other factors including volume of entrapped air, aggregate type and grading, and porous properties of used materials. Thus the presence of voids in concrete reduces the density and consequently reduces compressive strength: 5% of voids can reduce the compressive strength by as much as 30% (Neville and Brooks, 2004). Increasing water content is known to reduce density, as reported elsewhere (Nematzadeh and Naghipour, 2012).

The results also showed that the average density of the mortar mix with drinking water (M14) was comparatively higher than that made with RSS (M3), as the average density of M14 was 2130 Kg/m^3 and for M3 was 2072 Kg/m^3. For Series 2, the results showed that the average density of the control mix was comparatively higher than that with RSS (2099 Kg/m^3 for MLRef and 2023 Kg/m^3 for ML1). For Series 3 (concrete mixes), the results showed that the density of the control mix (CMRef) was significantly greater than that made with RSS (CM1), as the average density of CMRef was 2364 Kg/m^3 whereas the average density of CM1 was 2238 Kg/m^3. This may be due to the presence of the organic materials in the RSS and its impact on the overall density.

For the mortar mixes with RSS and different content of sand (Group 2), the results showed that the average density steadily increased when the sand content increased (up to sand to cement ratio of 6) for which the best average density of 2169 Kg/m^3 was recorded. This agreed with results reported elsewhere (Panyakapo and Panyakapo, 2008).

For the mortar mixes with unprocessed fly ash and RSS/Binder ratio of 0.65 (Group 3), the results showed that the average density decreased when the unprocessed fly ash content increased above 10% and the greatest average density of 2203 kg/m^3 was recorded for the mortar mix with 10% unprocessed fly ash (M2). For the mortar mixes with unprocessed fly ash and RSS/Binder ratio of 0.8 (Group 4), the average density steadily increased when the fly ash content increased (up to 20% cement replacement). The greatest average density of 2101 Kg/m^3 was recorded for the mortar mix with 20% unprocessed fly ash replacement (M9). The results also presented that the density decreased when the content of RSS/Binder ratio increased. For the mortar mixes with large proportions of unprocessed fly ash (Series 2), the results showed that the average density increased when cement was replaced by unprocessed fly ash at 40%, and the greatest average density of mortar mixes with RSS was recorded for ML2 at 2061 Kg/m^3. The average density for the other two mixes (ML3: 60% unprocessed fly ash and ML4: 80% unprocessed fly ash) steadily decreased with increasing the content of fly ash. For the concrete mixes (Series 3), the results showed that the average density increased when the content of unprocessed fly ash increased up to 15%, and the greatest average density of 2302 Kg/m^3 was recorded for CM3 (15% unprocessed fly ash replacement). In general the addition of unprocessed fly ash to cement-based materials reduces density, as fly ash has a lower relative particle density (2.30 typically) than Portland cements (3.12 typically). Replacing 30% of cement mass with unprocessed fly ash increases the total volume of cementitious material by 15%. However, the addition of unprocessed fly ash may improve the density by influencing water absorption properties of cement-based system, as the grading and particle size of used fly ash significantly contribute to the volume of voids that will generate (UKQAA, 2013a).

The TWA of mortar mixes with different RSS/cement ratios (Group 1) generally decreased with curing age for all mixes in this group. However, a clear trend in the average TWA was observed. The average TWA increased when the content of RSS increased and the greatest average TWA of 11.6% was recorded for the mortar mix with RSS/Cement ratio of 1 (M4). This came in line with the outcome of a previous study (Nematzadeh and Naghipour, 2012). There are three main mechanisms that govern transport properties in cement-based systems: permeability, diffusion and absorption. Permeability measures fluids flow under controlled pressure, whilst diffusion is the movement of ions due to concentration differences. Absorption can be defined as the ability of cementitious materials to take in water due to the capillary suction. All three mechanisms are mainly associated with the volume of pores and the connectivity of which they network (Martys and Ferraris, 1997;

Castro et al., 2011). The ingress of water and dissolved salts into concrete is mainly governed by the capillary absorption action (Castro et al., 2011; Spragg et al., 2011), and therefore, water absorption properties have been used as an important factor to evaluate durability properties of cement-based systems (Maltais et al., 2004).

Fresh cement paste consists of hydrates of the various cement components and of $Ca(OH)_2$, and the total volume of these products is the sum of the total volume of dry cement and the volume of mix water. As a result of the hydration process, mix water takes one of three forms including combined water, gel water and capillary water. The combined water almost represents 23% of the mass of the dry cement, which combines firmly (physically or chemically) to become non-evaporable water when subject to a high temperature of 105^oC. The gel water is the water proportion that is held physically or is adsorbed on the large surface area of the hydrated, and it almost represents 28% of the volume of the gel cement. Gel water is trapped in the gel pores between the solid hydration products, which are very small in size (about 2nm). Capillary water is held in the capillary voids that result from the hydration process, which are larger than the gel pores (about 1µm in size). For fully hydrated cement, with no excess water above the hydration requirements, capillary water represents 18% of the original volume of the cement. The capillary pores can be empty or filled with water, depending of the amount of mix water and depending also on whether additional water could inter the system during hydration (Mindess et al., 2003; Neville and Brooks, 2004).

The results also showed that the average TWA for the control mix (M14) was relatively higher than that for the mix with RSS (M3). TWA for the control mix was 10.1% and for M3 was 9.7%. For the mortar mixes with RSS and different sand content (Group 2), TWA generally decreased with curing age for all mixes in this group. However a clear trend in the average TWA was also observed, as the average TWA decreased when the sand content increased and the greatest average TWA of 12% was recorded for the mix with sand to cement ratio of 3 (M5). For the mortar mixes with large proportions of unprocessed fly ash (Series 2), the results showed no significant difference in TWA between the control mix (MLRef) and the mix that contained RSS (ML1). For the concrete mixes (Series 3), the results showed that the average TWA for the control mix (CMRef) was relatively higher than that with RSS (CM1), as the average TWA for CMRef was 6.5% and for CM1 was 6.1%.

For the mortar mixes with RSS and unprocessed fly ash, the results showed that TWA values were varying with curing age for all mixes. For Group 3, the average TWA increased steadily when unprocessed fly ash content was included and the greatest average TWA value of 9.1% was recorded for the mortar mix with 30% unprocessed fly ash (M13). For Group 4, the results showed that replacing cement with 10% unprocessed fly ash (M11) decreased TWA in comparison with the mix that contained 0% unprocessed fly ash (M2). However, the addition of unprocessed fly ash increased TWA for mixes with 20 and 30% unprocessed fly ash (M12 and M13 respectively). Additionally and in general, TWA increased when RSS content increased for all mixes with unprocessed fly ash. For mortar mixes with large proportions of unprocessed fly ash (Series 2), the addition of unprocessed fly ash generally increased the TWA values and the greatest average TWA of 15.7% was recorded for the mix with 80% unprocessed fly ash (ML4). For concrete mixes (Series 3), the results showed that the average TWA increased when unprocessed fly ash content increased up to 15% replacement, and the highest average TWA value of 6.6% was recorded for CM3 (15% unprocessed fly ash). This may be linked to the LOI value, which represents the amount of the observant unburned carbon that was presented in the unprocessed fly ash.

9.3 MECHANICAL PROPOERTIES

9.3.1 UPV

Ultrasonic Pulse Velocity (UPV) in a non-destructive test used in concrete and other solid construction materials to examine its quality and compressive strength. It employs an ultrasonic pulse to provide information on the uniformity of concrete, cavities, cracks and defects. The pulse velocity in any construction material depends on its density and its elastic properties including strength. Concrete quality can be classified based on UPV values: >4500 m/s is strong, 3500-4500 m/s is good, 200-3500 m/s is intermediate and <2000 m/s is weak (Whitehurst, 1951).

In this experimental work, UPV for the mortar mixes with different RSS/Cement ratios increased when the content of RSS was reduced at all curing ages. As UPV is a function of strength and porosity, previous studies came in line with these findings and confirmed that UPV values decrease when w/c ratio increased (Liu et al., 2011b; Al-Mufti and Fried, 2012). The results also showed that UPV values improved with time. However the greatest UPV values were not necessary achieved at 365 days, but at earlier ages (28 or 90 days). This was probably because of the changes in the structure of mortar with time due to the strength gain (Mannan et al., 2002). The subsequent falling in UPV at 365 days may be due to the fact that the rate of loss of moisture exceeded the gain in strength (Al-Sugair, 1995), or due to the change in chemical composition of the organic matter present in the RSS. UPV values for the control mix that was prepared with water (M14) were comparatively greater than those for the mix with RSS (M3). This may be again due to the presence of the organic matter in the RSS, which slowed down the pulse speed.

For mixes that incorporated RSS and different sand content, the results generally showed that UPV values increased when the sand content increased up to cement to sand ratio of 6 and the greatest UPV values were achieved at either 28 days or 90 days. UPV values declined at 365 days for all mixes in this group.

For the group of mortar mixes that incorporated unprocessed fly ash and RSS/Binder ratio of 0.65 (Group 3), the results showed that UPV values generally decreased when the content of unprocessed fly ash was increased at all curing ages in this group except at 28 days of the mix with 10% fly ash (M11). The maximum UPV values were achieved at either 90 days (M2: 0% unprocessed fly ash and M12: 20% unprocessed fly ash) or at 28 days (M11: 10% unprocessed fly ash and M13: 30% unprocessed fly ash). The results also presented that UPV values declined at 365 days for all mixes in this group. For Group 4, the results showed that UPV values at earlier ages (1 and 7 days) generally decreased when the content of unprocessed fly ash increased. At later ages (28 and 90 days) no significant differences in UPV was observed, but more improvement in the UPV was noticed at 365 days when unprocessed fly ash increased up to 20% replacement. Additionally, both Figure 5.3 and Figure 5.4 showed that UPV increased when RSS content reduced, as UPV values for mixes with RSS/Binder ratio of 0.65 were comparatively greater than those for the mixes with RSS/Binder ratio of 0.8, and this could be due to the increase in liquid content (Liu et al., 2011b; Al-Mufti and Fried, 2012).

For the control mixes, the results showed that UPV values at 1, 7 and 28 days decreased when unprocessed fly ash content increased and the greatest UPV readings were recorded for the mix with 0% fly ash (M14). At later ages (90 and 365 days), UPV values for the mortar mixes with unprocessed fly ash were comparatively greater than those for the mix without it, and the greatest UPV values were recorded at 365 days. The results also showed that UPV values continued to improve with curing age until 365 days except for the mix with 0% unprocessed fly ash (M14). This may be correlated to the long-term strength development resulted from the inclusion of fly ash (Bouzoubaa et al., 1998; Poon et al., 2000; Kearsley and Wainwright, 2001; Escalante-García and Sharp, 2005).

For the mortar mixes with large proportion of unprocessed fly ash, UPV generally decreased when unprocessed fly ash content increased. However some improvement in UPV values were observed for the mix with 40% unprocessed fly ash (ML2) at later age. For the concrete specimens, the results showed that the addition of unprocessed fly ash did not significantly influence UPV at all curing ages except at 1 day. The results also showed that UPV values of the control mix were comparatively greater than those for the mix with RSS, and this may be due to the influence of the organic matter present in the RSS.

9.3.2 Compressive Strength

For the mortar mixes that incorporated different RSS content, the results clearly showed that the compressive strength declined when the content of RSS increased. This agreed with the outcomes of previous researches, which confirmed that the compressive strength decreases when the w/c ratio increases (Butalia et al., 2001; Sebok et al., 2001; Su and Miao, 2003; Neville and Brooks, 2004; Liu et al., 2011b; Al-Mufti and Fried, 2012). Additional factor that might affect the compressive strength was the increase of the organic and inorganic impurities in mortar mixes when RSS content was included (Valls, 2000; Valls et al., 2004; Yagüe et al., 2005; Cheilas et al., 2007; Jianli et al., 2010). The results also showed that the compressive strength steadily developed with curing age until 90 days prior to its subsequent insignificant falling at 365 days (except for M4: RSS/Cement ratio 1). The subsequent falling in compressive strength at 365 days may be due to the fact that the loss rate of moisture exceeded the gain in strength (Al-Sugair, 1995), or due to the change in chemical composition of the organic matter present in the RSS. Moreover, compressive strength of the mortar mix that contained RSS (M3) was fairly good in comparison with the mix that contained drinking water (M14), as the compressive strength values of M3 were 56%, 62%, 60%, 71% and 72% of M14 at 1, 7, 28, 90 and 365 days respectively.

For the mortar mixes with RSS and different sand content (Group 2), the compressive strength at 7, 28, 90 and 365 days generally reduced when the sand content increased and the greater compressive strength was achieved for the mix with sand to cement ratio of 3 (M5), except at 90 days for the mix with sand to cement ratio of 6 (M6). At early age, specifically 1 day, the compressive strength increased when the sand content increased. Moreover, the results showed that the compressive strength continually developed with curing age until 90 days prior to its subsequent insignificant falling at 365 days.

For the mortar mixes with RSS and unprocessed fly ash (Group 3), the results presented that the compressive strength at early ages (1, 7 and 28 days) generally decreased when unprocessed fly ash content increased. At later ages (90 and 365 days) the results showed certain improvement in compressive strength when cement was replaced by unprocessed fly ash at 20% (except at 90 days for the mortar mix with 0% unprocessed fly ash). For Group 4, the compressive strength increased when unprocessed fly ash content was increased, and the greatest compressive strength values were achieved for the mortar mixes with 10 and 20% unprocessed fly ash (M8 and M9 respectively). The results also showed that that addition of unprocessed fly ash generally improved long-term strength development and successfully stopped the drop in strength that was observed in mixes without unprocessed fly ash at 365 days. This may be due to the positive impact of the pozzolanic activities present in fly ash on long-term strength development (Gebler and Kleiger, 1986; Tikalsky et al., 1988; Wild et al., 1995; Bouzoubaa et al., 1998; Lam et al., 1998; Poon et al., 2000; Kearsley and Wainwright, 2001; Escalante-García and Sharp, 2005).

For the control mixes (Group 5), the compressive strength at 1, 7, 28 and 90 days decreased when unprocessed fly ash content increased, and the greatest compressive strength was achieved for the mortar mix with 0% unprocessed fly ash (M14). At later ages (365 days) a noticeable improvement in compressive strength for all mixes that contained unprocessed fly ash was observed, and the greatest compressive strength of 26.4 MPa was recorded for the mix with 10% unprocessed fly ash (M15). The results also showed no significant differences in strength between mixes that contained RSS and those made with water when unprocessed fly ash was added in this group.

For the mortar mixes that contained RSS and large proportion of unprocessed fly ash, the results showed that compressive strength increased when unprocessed fly ash content decreased at all ages. The results also demonstrated that compressive strength of the control mix was comparatively greater than that for the mix with RSS.

For the concrete mixes, the compressive strength at 1 and 7 days generally decreased when the unprocessed fly ash content increased. At later ages (28 days) the results showed a certain improvement in compressive strength when cement was replaced with unprocessed fly ash at 10-20%. The results also showed that replacing cement with unprocessed fly ash at 15% significantly improved long-term compressive strength (90 and 300 days). Moreover, the compressive strength of concrete mix that contained RSS (CM1) was fairly good in comparison with the mix that contained drinking water (MCRef), as the compressive strength values of CM1 were 90%, 68%, 56%, 62% and 64% of CMRef at 1, 7, 28, 90 and 300 days respectively.

9.3.3 Flexural Strength

For the mortar mixes with different RSS content (Group 1), the results showed a clear trend in flexural strength with RSS content, as strength decreased when the content of RSS increased, except for the mortar mix with RSS/Cement ratio of 0.8 (M3) at 90 and 365 days. The greatest flexural strength was recorded for the mortar mix with RSS/Cement ratio of 0.5 (M1) at all curing ages. This came in line with the outcomes of previous research (Haach et al., 2011; Wu et al., 2012; Singh and Siddique, 2013). Although the flexural strength development with curing age was not substantial, the results showed continued development in strength until later ages up to 365 days. No significant differences in flexural strength were observed between the mortar mix with RSS (M3) and the control mix with water (M14) at 7 and 365 days. However, some minor differences were detected at other curing ages (28 and 90) days.

For the mortar mixes with RSS and different unprocessed fly ash content (Group 3), the flexural strength at 7 and 28 days decreased when the content of unprocessed fly ash increased and the best strength was recorded for the mortar mix with 0% unprocessed fly ash (M2). This may be due to the fact that the cement is severely diluted by unprocessed fly ash and the hydration action was therefore delayed (Cao et al., 2000). At later ages (90 and 365 days), the flexural strength was improved when unprocessed fly ash was added at 10 and 20% replacement, and the greatest strength at 90 days was recorded for the mix with 10% unprocessed fly ash (M11) and at 365 days was recorded for the mortar mix with 20% unprocessed fly ash (M12). This can be interpreted due to the positive contributions of fly ash on long-term strength (Siddique, 2003). For the Group 4, the results showed that no significant improvement in flexural strength was achieved when unprocessed fly ash was included, and the greatest flexural strength was recorded for the mortar mix with 0% unprocessed fly ash (M3) at all curing ages.

For the control mixes (Group 5), no significant improvement in flexural strength was observed when unprocessed fly ash was included, and the greatest flexural strength was recorded for the mortar mix with 0% unprocessed fly ash (M14) at all curing ages. In addition, no significant differences in flexural strength were observed between the mortar mixes with RSS (M3, M8, M9 and M10) and the control with water (M14, M15, M16 and M17).

For the concrete mixes, the results clearly demonstrated that the addition of unprocessed fly ash had a positive impact, as flexural strength increased when the content of unprocessed fly ash also increased and the greatest strength was recorded for the mortar mix with 20% unprocessed fly ash (CM4). It was also observed that the flexural strength of the control mix with water (CMRef) was not significantly greater than that for the mix with RSS (CM1).

9.3.4 Drying Shrinkage

For the mortar mixes that contained different RSS content (Group 1), drying shrinkage generally increased when the content of RSS increased and this can be clearly seen for the mortar mixes with RSS/Cement ratio 0.5, 0.65 and 0.8 (M1, M2 and M3 respectively). This agrees with the findings of other studies, which confirmed that drying shrinkage increases when the water content is increased (Hover, 2011; Singh and Siddique, 2013; Zhang et al., 2013). The results also showed that most of the drying shrinkage occurred during the first

50- 70 days. Moreover, no significant difference in drying shrinkage was observed between the control mix (M14) and its corresponding mix that was made with RSS (M3).

For the mortar mixes with RSS and different proportions of unprocessed fly ash, it was noticed that the drying shrinkage decreased when the content of unprocessed fly ash increased for both Group 3 and Group 4 (RSS/Binder ratios of 0.65 and 0.8 respectively). This may be due to the positive influence of including fly ash on drying shrinkage values, as the fine particles that are present in fly ash fill in the voids and consequently reduce the shrinkage (Atis et al., 2004; Yazici et al., 2005; Chau et al., 2009). The results also showed that drying shrinkage of the mortar mixes that made with RSS/Binder ratio of 0.65 was comparatively less than those made with higher RSS/Binder ratio of 0.8.

For the control mixes that contained water and different ratios of unprocessed fly ash (Group 5), drying shrinkage mostly occurred in the first 50 days, during which no significant differences were observed. At later ages, the results generally showed that drying shrinkage decreased when unprocessed fly ash content increased.

For the concrete mixes, the results demonstrated that drying shrinkage decreased when unprocessed fly ash content increased for all mixes in this series. It was also observed that drying shrinkage increased when water was replaced with RSS.

9.4 SULPHATE RESISTANCE (SULPHATE ATTACK)

The durability of cement-based materials subjected to aggressive environments is largely dependent on the pore system, which directly influences transport and leaching properties (Maltais et al., 2004; Henkensiefken et al., 2009; Castro et al., 2011). There are three main mechanisms that govern transport properties in cement-based systems: permeability, diffusion and absorption. Permeability measures fluids flow under controlled pressure, whilst diffusion is the movement of ions due to concentration differences. Absorption can be defined as the ability of cementitious materials to take in water due to the capillary suction. All three mechanisms are mainly associated with the volume of pores and the connectivity of which they network (Martys and Ferraris, 1997; Castro et al., 2011). The ingress of water and dissolved salts into concrete is mainly governed by the capillary absorption action (Castro et al., 2011; Spragg et al., 2011), which plays a significant role in concrete deformation due to sulphate attack.

Cement hydration process produces comparatively greater amounts of portlandite $Ca(OH)_2$ than both Class C and Class F fly ashes. The reaction of cement hydration products with sulphate is likely to produce more gypsum ($CaSO_4$) and more ettringite ($C3A{\cdot}3CaSO_4{\cdot}32H_2O$), which are responsible for more expansion (Rozière et al., 2009). There are typically two types of sulphate attack: the first one is resulting from the reaction of sulphate with calcium hydroxide to produce gypsum (reaction 9.1); the second type is resulting from the reaction of alumina-bearing hydration products, and/or unhydrated tricalcium aluminate (C_3A) with sulphate and thus ettringite is produced as shown in reaction 9.2 (Manu et al., 2003).

$$Ca(OH)_2+Na_2SO_4.10H_2O \longrightarrow CaSO_4.2H_2O+2NaOH+8H_2O \qquad \text{Reaction 9.1}$$

$$2(3CaO.AL2O3.12H2O)+3(Na2SO4.10H2O) \longrightarrow$$
$$3CaO.AL_2O_3.3CaSO_4.31H_2O+2AL(OH)_3+6NaOH+17H2O \qquad \text{Reaction 9.2}$$

In this experimental work, the results showed that sulphate attack resistance of mortar specimens that contain different RSS content weakened when the content of RSS increased. This is clearly due to the high void content generated as a result of using higher liquid to cement ratios (Neville and Brooks, 2004). The best result of sulphate attack resistance was therefore recorded for the mortar mix with the lowest RSS/Cement ratio of 0.5 (M1). The results also showed that sulphate attack resistance of both mortar and concrete specimens made with water were comparatively better than those made with RSS. This may be due to the negative influence of the organic matter presented in RSS, which from one side increased voids and from the other side weakened the overall strength (refer to sections 4.7.2 and 5.5.2).

For both mortar and concrete mixes that contained unprocessed fly ash, the results clearly demonstrated that the inclusion of unprocessed fly ash significantly improved sulphate attack resistance for specimens with both RSS and water. For the mortar mixes that contained RSS, the best results were recorded for the mixes with 30% unprocessed fly ash replacement for both RSS/Binder ratios (0.65 and 0.8). For the concrete mixes, the best results were recorded when the cement was replaced by 20% unprocessed fly ash. This came in line with other research findings, which concluded that the incorporation of unprocessed fly ash products into the cement-based system positively improved sulphate resistance (Dikeou, 1970; Harmann and Mangotich, 1987; Tikalsky and Carrasquillo, 1989; Dhole et al., 2009).

There is a strong correlation between the sulphate resistance of cement-based products and its tricalcium aluminate (C_3A) content. The higher the C_3A content, the weaker the concrete to sulphate attack. The sulphate resistance of cement-based materials can be improved by lowering the content of C_3A. ASTM C 150/C 150M-12 (ASTM, 2012a) specifies two types of Portland cement that are typically suitable for sulphate resistance. Type II cement contains less than 8% total weight C_3A, and Type V with less than 5% C_3A total weight. Alternatives include partial replacement of Portland cement with pozzolanic materials such as low calcium fly ash, ground granulated blast furnace slag, or silica fume equally to reduce the potential for sulphate attack. The pozzolans consume the calcium in the pore water, and consequently reduce the total mass of C_3A and decrease the permeability. When deciding which pozzolan to add, it is essential to consider its CaO content, as a high content of CaO may speed up the sulphate problem substantially. Similarly, silica fume, met kaolin and natural pozzolans consume Ca to improve sulphate resistance (Mangat and Khatib, 1995; Khatib and Wild, 1998; Penn State University, 2014).

There are several steps involved in the pozzolanic reaction in cement-based materials. When Portland cement mixed with water, the tricalcium silicate (C_3S) and dicalcium silicates (C_2S) react to form calcium silicate hydrates (C-S-H), which is mainly responsible for the strength development, together with calcium hydroxide, $Ca(OH)_2$. Consequently, the alkalinity of the water (pore fluid) increases to pH 13 or higher providing the ideal conditions for the pozzolan to react. The raised pH first causes the silicate network structure of the pozzolan to break down to smaller units. Thereafter it reacts with the calcium hydroxide to form additional calcium silicate hydrate binder. This process converts the calcium hydroxide (which has no strength-forming properties) in the cement-based materials to additional C-S-H binder that is deposited in pore spaces. Consequently, this leads to an increase in strength, a reduction in permeability, and an improvement in long-term durability (minerals, 2014).

9.5 ENVIRONMENTAL PROPERTIES (LEACHING TEST)

Stabilisation/solidification is a process widely applied for the immobilization of hazardous substances present in wastes, especially for metals, and cement is the most common binder that used for this purpose. Zeolites can also be used, in addition to Portland cement, to stabilise/solidify hazardous wastes containing high levels of metals such as mercury (Zhang et al., 2009). This technology was effectively applied, using Portland cement, for solidification/stabilisation of contaminated soils with metals including Cd, Pb, Zn, Cu, Ni and As (Voglar and Lestan, 2010). Cement kiln dust and Portland cement were used, as a binder, to solidify and treat artificial soil contaminated with selenium (Se) (Moon et al., 2009). Ordinary Portland cement and other replacements, such as oil palm ash, were used to treat industrial sludge containing nickel hydroxide (Yin et al., 2008). Other types of cement, such as alkali-activated cements, were presented and used to treat radioactive wastes (Shi and Fernandez-Jimenez, 2006). Fly ash products were also used in addition to cement to treat different types of hazardous wastes including heavy metals, contaminated soils, and marine sediments (Singh and Pant, 2006; Qian et al., 2008; Zentar et al., 2012; Kogbara et al., 2013).

The concentrations of pollutants in the test leachant are significantly dependant on a number of interacting factors including volume of leachant, curing time of the test specimen, immersion time (eluate collection intervals), concentration of pollutants in the test specimens, nature of pollutants, structure of the binding system, and testing accuracy/errors. A number of testing variables were therefore fixed for this part of the experimental work and those are as follows;

- The volume of the test leachant was calculated as per Equation 7.1 above
- Two 50 mm in size mortar cubes were cured for 28 days
- Three emersion times (eluate collection intervals) of 2 hours, 8 days and 28 days were selected
- Mixing proportions were as shown in Table 3.7.
- ICS and ICP tests were performed.

The concentrations of detected pollutants are summarised in Table 9.1. The table clearly shows a safe level of heavy metals concentration presented in the leachant. The concentrations of detected heavy metals mostly meet the requirements of the Surface Water Regulations and/or the EU Drinking Water Directive (Appendix B). However, the results showed higher concentrations of a number of heavy metals including Se, As, Cr and Pb, which exceeded the requirements of both Water Regulations and the EU Drinking Water Directive. The EU Ground Water Directive included Se, As, Cr and Pb on List II of the hazardous substances that might have a harmful impact of the surrounding environment. Although the directive does not specify the allowable concentrations of list II substances, it firmly stated that effective protection measures must be in place in order to protect ground water. Authorities therefore must ensure preventing the discharge of substances on list I and limiting the discharge of substances on list II (EUR-Lex, 2013). The ICS analyses showed safe concentrations of all ions except Phosphate, which in some readings exceeded the requirements of the Surface Water Regulations. However, Phosphate was included on list II of the EU Groundwater Directive.

The effectiveness of using Portland cement and fly ash in retaining heavy metals may be due to the ionic adsorption nature of the hydrate C–S–H in the hydrated cement products. The ionic attachment of the heavy metals to the crystalline network of some products of the hydration process such as sulphates in the ettringite, physically retain them in the porous structure (Cheilas et al., 2007; Malliou et al., 2007). The retention of heavy metals may also be due to the good distribution of the binding materials (cement and/or fly ash) in the cement-based systems, which enables regular and strong bond between heavy metals and the hydration products (Valls, 2002). The presence of sulphates in the leachant (the water in direct contact with the test specimens) may due to the surface wash of the hydrated sulphates formed in the cement hydration process, such as ettringite (Valls, 2002). The retention of chlorides in the hydrated cement is due to the formation of monochloroaluminates of calcium (Friedel's salt: $3CaO.Al_2O_3.CaCl_2.10H_2O$), which can chemically hold a considerable proportion of chlorides when present in high concentrations (N., 1989).

The outcome of this part of the experimental work showed that using cement-based materials was significantly efficient in retaining pollutants presented in both RSS and unprocessed fly ash. This came in line with the outcomes of previous research that was undertaken in the area of using cement products to solidify different waste materials including sewage sludge (Valls, 2002; Cyr et al., 2007; Samaras et al., 2008). However, it must be kept in mind that more environmental test must be performed before any large scale use is undertaken.

Table 9.1: Concentrations of detected heavy metals and ions.

Pollutants	Detected concentrations (PPM)	Mix	Notes	Quality/Standard*
Al	3.84, 3.47, 2.48, 1.99, 2.06, 3.02, 3.1, 2.94, 3.34, 5.13, 4.79, 4.83, 5.34, 0.89, 4.35, 3.92 & 4.65	M1, M2, M3, M4, M5, M6, M7, M8, M9, M10, M11, M12, M13, M14, M15, M16 & M17 respectively	The detected concentration is significantly below the requirements of the EU Drinking Water Directive of 200 mg/l (PPM).	EU Drinking Water Directive
Fe	0.48, 0.02, 0.01, 0.02, 0.01 & 0.01	M1, M2, M3, M6, M7 & M9 respectively	The highest detected concentration meets the requirements of the Surface Water A2 and A3 categories. Other concentrations meet the requirements of the EU Drinking Water Directive.	Surface water A2 and A3, and EU Drinking Water Directive
Co	0.23	M1	No requirements	Drinking Water Directive
Ni	0.27, 0.05, 0.06 & 0.26	M1, M5, M9 & M12 respectively	The detected concentrations exceeded the EU Drinking Water Directive requirements of 0.02 PPM. No requirements for the Surface Water Regulations.	Surface Water Regulations.
Cu	0.45 & 1.65	M1 & M12 respectively	The detected concentration meets the requirements of the Drinking Water Directive.	Drinking Water Directive
Zn	0.4	M1	The detected concentration meets the requirements of the Surface Water Regulations. No requirements for the Drinking Water Directive.	EU Drinking Water Directive
Mn	0.2	M1	The detected concentration meets the requirements of both A2 and A3 waters	Surface Water Regulations (A2 and A3 waters)
Ba	0.26, 0.23, 0.17, 0.2, 0.14, 0.12, 0.08, 0.19, 0.1, 0.19, 0.3, 0.62, 0.14, 0.1, 0.13 & 0.08	M1, M2, M3, M4, M5, M6, M7, M8, M9, M10, M11, M12, M13, M15, M16 & M17 respectively	The detected concentration meets the requirements of both A2 and A3 waters	Surface Water Regulations (A2 and A3 waters)
Se	0.21, 0.04, 0.04, 0.2, 0.16 & 0.08	M8, M9, M12 M15, M15 & M17 respectively	The detected concentrations exceeded the requirements of both the Surface Water Regulation and the EU Drinking Water Directive.	Groundwater Directive
As	0.58 & 0.06	M1 & M15 respectively	The highest detected concentration exceeded the requirements of both the Surface Water Regulations and the EU Drinking Water Directive. The other concentration meets the requirements of A3 waters of 0.1 PPM.	Groundwater Directive
Mo	1.02, 0.13, 0.06, 0.04, 0.04, 0.3, 0.05, 0.04, 0.04, 0.28, 0.030.04, 0.04 & 0.04	M1, M2, M3, M4, M5, M7, M9, M11, M12, M13, M15 M16 & M17 respectively	No Requirements for both the Surface Water Regulations and the EU Drinking Water Directive. This element was included on list II of the Groundwater Directive.	Drinking Water Directive
Cr	0.82, 0.11, 0.1, 0.1, 0.1, 0.1, 0.1, 0.1, 0.1, 0.1, 0.1, 0.1, 0.1, 0.1, 0.1, & 0.1	M1, M2, M3, M4, M5, M6, M7, M8, M9, M10, M11, M12, M13, M15, M16 & M17 respectively	The detected concentrations exceeded the requirements of both the Surface Water Regulations and the EU Drinking Water Directive of 0.05 PPM.	Groundwater Directive
Pb	0.12, 0.02, & 0.08	M8, M9 & M15 respectively	M8 & M15 exceeded the requirements of both the Surface Water Regulations and the EU Drinking Water Directive. M9 meets the requirement of A1 waters. This element was included on list II of the Groundwater Directive.	Groundwater Directive
Sn	2.03, 0.59, 1.12, 0.15, 0.2, 0.06, 0.05, 2.2, 0.75, 0.51, 0.13 & 0.44	M1, M2, M3, M4, M5, M7, M8, M10, M12, M15, M16 & M17 respectively	No Requirements for both the Surface Water Regulations and the EU Drinking Water Directive. This element was included on list II of the Groundwater Directive.	Drinking Water Directive
Bromide	1.05, 0.26, 1.21, 0.63, 0.46, 0.26 & 0.22	M3, M4, M5, M7, M10, M13 & M16 respectively	No requirements	The Drinking Water Directive
Chloride	3.95, 6.53, 19.21, 2.6, 3.31, 5.34, 2.57, 11.15, 2.21, 6.39, 4.9, 5.81, 10.85, 8.22, 3.08, 7.2 & 7.36	M1, M2, M3, M4, M5, M6, M7, 8, M9, M10, M11, M12, M13, M14, M15, M16 & M17 respectively	The detected concentrations meet the requirements of A1, A2 & A3 waters of 250 PPM. No requirements of the EU Drinking Water Directive.	The Drinking Water Directive
Fluoride	0.37, 0.45, 0.4, 0.38, 0.36, 0.46, 0.43, 0.34, 0.34, 0.68, 0.43, 0.49, 0.31, 0.43, 0.4 & 0.61	M1, M2, M3, M4, M5, M6, M7, M8, M9, M10, M11, M12, M13, M15, M16 & M17 respectively	The detected concentrations meet the requirements of the EU Drinking Water Directive of 1.5 PPM.	The Drinking Water Directive
Nitrite	0.46, 0.26, 0.24, 3.34, 2.2 & 0.61	M2, M3, M4, M10, M16 & M17	The concentrations of M10 & M17 exceeded the requirements of the EU Drinking Water Directive of 0.5 PP.	Surface Water Regulations
Nitrate	1.37, 0.21, 1, 1.38, 1.66, 3.74, 3.43, 4.1, 2.33, 0.16, 3.33, 1.22, 6.16, 5.48, 1.1, 2.46 & 3.93	M1, M2, M3, M4, M5, M6, M7, M8, M9, M10, M11, M12, M13, M14, M15, M16, M17 respectively	All detected concentrations meet the requirements of the EU Drinking Water Directive of 50 PPM	The Drinking Water Directive
Phosphate	19.27, 1.54, 1.15, 6.25, 0.38, 0.64 & 0.52	M2, M7, M11, M12, M13, M15 & M16 respectively	Detected concentrations for M2, M7, M11 & M12 exceeded the requirements of the Surface Water Regulations of 0.7 PPM. No requirements for the EU Drinking Water Directive. This ion was included on list II of the Groundwater Directive	• The Groundwater Directive.
Sulphate	19.27, 8.89, 2.28, 7.57, 5.29, 6.57, 15.44, 5.06, 15.71, 7.68, 0.29, 9.47, 7.6, 4.11, 9.3 & 14.46	M2, M3, M4, M5, M6, M7, M8, M9, M10, M11, M12, M13, M14, M15, M16 & M17	All detected concentrations meet the requirements of the EU Drinking Water Directive of 250 PPM.	The Drinking Water Directive

*** The requirements of the EU Drinking Water Directive, Surface Water Regulations and Ground Water Directive are presented in Appendix B.**

9.6 CORRELATION BETWEEN DIFFERENT PROPERTIES

9.6.1 Compressive strength with UPV

The results revealed that the compressive strength strongly correlated with UPV for both the mortar mixes and concrete mixes (R^2 ranged between 0.65 and 0.95).

For the mortar mixes with different RSS content, the compressive strength related strongly to the UPV and a clear trend was observed. The compressive strength increased when the UPV increased and R2 value was 0.86. As UPV is a function of strength and porosity (Liu et al., 2011b; Al-Mufti and Fried, 2012), the results showed that UPV increased when the moist content decreased and this was also reported in Chapter 5 (Figures 5.1 and 5.12). This finding agreed with the outcomes of previous researches, which confirmed similar correlation (Albano et al., 2009; Her-Yung, 2009; Rahmani et al., 2013). The effect of varying the sand content on the relationship between compressive strength and UPV was studies. The results showed a clear trend between those properties and confirmed that compressive strength increased when the UPV increased for all sand contents. Less correlation was observed for this group and R^2 value was 0.65.

For the mortar mixes with different unprocessed fly ash and different RSS content, it was evident that the compressive strength relates strongly with the UPV, as R^2 values ranged between 0.83 and 0.86. The control mixes (Group 5) showed even a stronger correlation, as R^2 value was 0.95. For the concrete mixes, the correlation between the compressive strength and UPV was strong and R^2 value was 0.89.

The relationship between the compressive strength and UPV was expressed using an exponential curve, which in most cases gave the best fit line (the greatest R^2). The literature confirmed that this type of function was also used in previous studies (Demirbog et al., 2004; Khatib, 2005; Khatib, 2008b; Khatib, 2008a; Atici, 2011; Kou et al., 2012). Nevertheless, other functions were also used to express this relationship including power functions (Demirbog et al., 2004; Khatib, 2005; Khatib, 2008b; Khatib, 2008a; Atici, 2011; Kou et al., 2012; Sua-iam and Makul, 2013; Yap et al., 2013), linear functions (Mo et al., 2014), and polynomial functions (Uysal and Yilmaz, 2011).

9.6.2 Compressive strength with TWA

Since the presence of voids in concrete reduces the density and consequently reduces compressive strength (Neville and Brooks, 2004), TWA test was carried out on both mortar and concrete mixes in order to determine the percentage of voids and to indirectly assess the porosity. In previous Chapters, the influence of varying different parameters on TWA and compressive strength were discussed individually. However, this part of the work discussed the correlation between both properties and used a power function to expresses the relationship between them.

For the mortar mixes with different RSS content, it was observed that compressive strength was fairly depending on TWA (R^2=0.55), as the compressive strength increased when the values of TWA decreased. It was also noted that TWA increased with increasing the content of RSS. These findings were presented in Figure 4.23.

For the mortar mixes with different sand content, the analysis showed a clear trend and presented that compressive strength increased with the reduction of TWA. It also showed that TWA increased when the cement content increased, which is due to the generation of voids during the hydration process of cement products (Neville and Brooks, 2004). The correlation for this group was not very strong and R^2 value was 0.03.

Compressive strength also correlated fairly with TWA for the mortar mixes with different unprocessed fly ash content and different RSS content, as the strength related negatively with the TWA for all mixes in these groups. R^2 values ranged between 0.28-0.29. For the control mixes, the same trend was observed and R^2 value was 0.27. The concrete mixes also showed that the compressive strength correlated negatively with TWA. R^2 value for this series was 0.39.

This work suggested a power function to correlate the compressive strength with TWA. This function was also used in previous studies that related the compressive strength with porosity (Poon et al., 2006; Chindaprasirt and Rukzon, 2008; Rukzon and Chindaprasirt, 2012). Other functions were also used including exponential functions (Lian et al., 2011), and linear functions (Menadi et al., 2009; Chen et al., 2012).

9.6.3 Flexural strength with compressive strength

The relationship between the flexural strength and compressive strength was analysed. The results presented that flexural strength is a function of compressive strength, and accordingly a strong correlation was observed. The flexural strength was significantly influenced by the content of the RSS and consequently decreased when the moist content increased. R^2 value for the mixes with different RSS content was 0.77.

For the mortar mixes with unprocessed fly ash, the results also demonstrated a strong correlation between flexural strength and compressive strength for both RSS contents. R^2 values ranged between 0.83-0.84. The same correlation was observed for the control mixes and R^2 value was 0.71. A relatively strong correlation was also noticed for the concrete mixes (R^2=0.74).

This analytical work proposed a power function to relate the flexural strength with compressive strength, which agreed with the suggestion of some previous works (Atis, 2005; Shafigh et al., 2012). Other research suggested different formulas including linear functions (Kenai et al., 2008; Dehwah, 2012; Jalal et al., 2013), and logarithmic functions (Nazari and Riahi, 2011).

9.6.4 Multiple regression

In addition to the curing age, compressive strength is a function of other factors including RSS content, sand content and unprocessed fly ash content. This study therefore attempted to correlate more than one parameter with the compressive strength. For all mixes, it was observed that the best fit curve that relates the compressive strength with curing age was a logarithmic (with the greatest R^2 value). This study therefore proposed a logarithmic function, as a core function, which was further expanded to include the influence of the other parameters. For each group of mixes, the equation coefficients were correlated with the main variable and a formula was then derived for each coefficient.

The results showed that the predicted compressive strength values were considerably close to the experimental ones, and this was clearly presented in Figures 8.26, 8.29, 8.32, 8.35, 8.38 and 8.41. All figures showed that the gradient values of the best fit line were considerably close to 1 (ranged between 0.9065 and 0.9719), and R^2 values ranged between 0.81 and 0.97.

CHAPTER 10: CONCLUSIONS, APPLICATIONS, LIMITATIONS AND FUTURE RECOMMENDATIONS

10.1 CONCLUSIONS

This research programme has examined and investigated the performance of cement-based materials containing Raw Sewage Sludge (RSS) as a water replacement and unprocessed fly ash as cement replacement. Three series of cement-based materials were investigated including mortar mixes with RSS and unprocessed fly ash (Series 1), mortar mixes with RSS and large proportions of unprocessed fly ash (Series 2), and concrete mixes with RSS and unprocessed fly ash (Series 3). Investigated mixes were tested for their fresh and physical properties (flowability/workability, density and total water absorption), mechanical properties (ultrasonic pulse velocity, compressive strength, flexural strength and length change due to drying shrinkage), durability properties (sulphate attach), and environmental properties (leaching test).

The results from the experimental work form the contributions to knowledge and were encouraging in that mortar and concrete mixes containing RSS and unprocessed fly ash that were produced showed comparatively good engineering, durability and environmental properties in comparison to the control. RSS can be used as a water replacement in mortar and concrete mixes with and without unprocessed fly ash. However, and in spite that the inclusion of unprocessed fly ash significantly reduced flowability/workability, it improved long-term compressive strength. It also prevented the reduction in compressive strength observed at 365 days for the mortar mixes with RSS only. The best long-term compressive strength was recorded for the mortar mixes with 10-20% unprocessed fly ash of total binder mass. For the concrete mixes, the greatest compressive strength at 300 days was recorded for the mix with 15% unprocessed fly ash replacement. The compressive strength of the mortar and concrete mixes with RSS was noticeably less than that of the mixes with water. The relative compressive strength for the mortar mixes ranged between 56-74% for 0% unprocessed fly ash, 75-99 for 10% unprocessed fly ash, 78-105% for 20% unprocessed fly ash, and 75-97% for 30% unprocessed fly ash. For the concrete mixes, the relative compressive strength ranged between 56-90%. The inclusion of higher proportions of unprocessed fly ash (40-80% total binder mass) significantly reduced compressive strength in comparison to the mix with 0% unprocessed fly ash.

The use or RSS as a water replacement did not significantly affect the density of mortar and concrete mixes in comparison to the control. The density values of the mortar mixes containing RSS ranged between 94.4-98.2% of those made with water. For the concrete mixes with RSS, the density ranged between 94.1-95% of the mix with water. The inclusion of unprocessed fly ash decreased the density of the mortar mixes with RSS/Binder ratio of 0.65. However, the density of the mortar mixes with higher Liquid/Binder ratio (0.8) generally improved when cement was replaced by 10-20% unprocessed fly ash of total binder weight for both mixes with RSS and water. For the concrete mixes, the addition of 15% unprocessed fly ash generally improved the density at all curing ages. TWA of the mortar mixes with RSS was generally less than that of the mixes with water. The average TWA values of the mortar mixes with RSS ranged between 89.9-96.9% of the mixes with water. The inclusion of unprocessed fly ash increased TWA at all curing ages and the greatest TWA readings were recorded for the mortar mixes with 30% unprocessed fly ash replacement with both RSS and water. The addition of unprocessed fly ash also increased TWA for the concrete mixes. For the UPV, the results showed no significant difference in UPV readings of the mortar mixes with RSS in comparison to those made with water. The relative UPV values ranged between 87.2-97% for 0% unprocessed fly ash, 88.4-99% for 10% unprocessed fly ash, 88.6-109.4% for 20% unprocessed fly ash, and 87.2-106.9% for 30% unprocessed fly ash. The inclusion of unprocessed fly ash generally reduced UVP values at earlier ages. However, adding 10-30% unprocessed fly ash improved UPV at 365 days for mortar mixes with both RSS and water. For the concrete mixes, the results showed that the addition of unprocessed fly ash did not significantly influence UPV at all curing ages except at 1 day (UPV decreased when unprocessed fly ash was added up to 15% of total binder weight). The UPV values of the control mix were slightly greater than those for the mix with RSS and the relative UPV ranged between 93.7-97.3%.

The use of RSS as a water replacement did not significantly affect the flexural strength in comparison to the control at 28, 90 and 365 days. The relative flexural strength for these curing ages ranged between 88-101% for 0% unprocessed fly ash, 86-103% for 10% unprocessed fly ash, 95-104% for 20% unprocessed fly ash, and 96-103% for 30% unprocessed fly ash. The inclusion of the unprocessed fly ash slightly improved long-term flexural strength for the mortar mixes with RSS/Binder ratio of 0.65. However, it reduced the flexural strength at all curing ages for the mortar mixes with higher Liquid/Binder ratio (both RSS and water). For the concrete mixes, the results revealed that the inclusion of unprocessed fly ash improved the flexural strength, and the greatest result was recorded for the mix with 15% unprocessed fly ash. The results also showed that the flexural strength of the control mix (CMRef) was relatively greater than that of the mix with RSS. The relative flexural strength was 79%.

The incorporation of unprocessed fly ash noticeably reduced length change due to drying shrinkage of both mortar and concrete mixes at later ages. The drying shrinkage mostly occurred in the first 50-70 days, during which no significant differences were observed when unprocessed fly ash was added. No substantial differences in drying shrinkage was observed between the mortar mixes with RSS and water. For the concrete mixes, the drying shrinkage of the control was slightly less than that of the mix with RSS.

Sulphate attack resistance of mortar and concrete mixes with both RSS and water significantly improved when unprocessed fly ash was included. No signs of deterioration were observed throughout the course of the test when cement was replaced by 30% unprocessed fly ash for the mortar mixes, and 20% unprocessed fly ash for the concrete mixes. The results also showed that the compressive strength of concrete and mortar samples, with the unprocessed fly ash content stated above, continued to improve with time despite being fully immersed in the sulphate solution.

The use of both RSS and unprocessed fly ash in cement-based systems showed no signs of significant pollution to the surrounding water, and safe levels of heavy metals and ions were detected in the water in direct contact with the test specimens when leaching test was performed. The quality of the leachant was checked against the requirements of the Surface Water Regulations, EU Drinking Water Directive, and EU Ground Water Directive. The quality of the leachant met the requirements of the EU Ground Water Directive.

10.2 APPLICATIONS

Cement-based materials containing RSS and unprocessed fly ash that were tested throughout this experimental work can be used in different construction and civil engineering applications, and as follows:

- Masonry mortar for external applications

Mortar mixes containing RSS and unprocessed fly ash can be utilised as a masonry mortar for use in masonry walls, columns and partitions. Masonry mortar can be used for different applications including bedding, jointing, pointing, facing & rendered masonry, and load bearing or non-load bearing masonry structures for building & civil engineering. According to BS EN 998-2:2010 (BSI, 2010b), masonry mortars can be categorised based on their compressive strength at 28 days into a number of classes, as shown in Table 10.1.

Table 10.1: Mortar classes (BSI, 2010b).

Class	M 1	M 2,5	M 5	M 10	M 15	M 20	M d
Compressive strength MPa	1	2.5	5	10	15	20	d
d is a compressive strength greater than 20 MPa as a multiple of 5 declared by the manufacturer.							

The compressive strength of the mortar mixes containing RSS with/without unprocessed fly ash that were investigated ranged between 8.3-36 MPa (Table 5.7). This primarily shows that M5 and above classes can be produced using RSS. The compressive strength of the mortar specimens was obtained using 50 mm in size cubes that comply with ASTM C109/C109M-08 (ASTM, 2008). However, BS EN 998-2:2010 requires that the compressive strength is to be obtained using 40x40x160 mm prisms that comply with the requirements of BS EN 1015-11: 1999 (BSI, 1999b). Therefore, further standard tests are required to be performed prior to any large scale application.

- <u>In-situ concrete for external applications</u>

This experimental programme investigated mechanical properties of a series of concrete mixes containing RSS and unprocessed fly ash. Mechanical properties mainly included compressive strength at 28 days of 100mm in size cubes in accordance to BS EN 12390-3:2009 (BSI, 2009b). BS EN 206: 2013 categorises concrete products based on their compressive strength into a number of classes, as listed in Table 10.2 (BSI, 2013a).

Table 10.2: Compressive strength classes for normal-weight and heavy-weight concrete (BSI, 2013a)

Compressive strength class	Minimum characteristic cylinder strength in MPa	Minimum characteristic cube strength in MPa
C8/10	10	8
C12/15	12	15
C16/20	16	20
C20/25	20	25
C25/30	25	30
C30/37	30	37
C35/45	35	45
C40/50	40	50
C45/55	45	55
C50/60	50	60
C55/67	55	67
C60/75	60	75
C70/85	70	85
C80/95	80	95
C90/105	90	105
C100/115	100	115

The 28 days compressive strength of tested concrete specimens ranged between 23.7-31.6 MPa (Table 5.11). Although BS EN 206: 2013 requires that the compressive strength has to be obtained using 150mm in size cubes, the results primarily showed that C16/20, C20/25 and C25/30 concrete classes can be produced using RSS and unprocessed fly ash. Concrete mixes containing RSS and unprocessed fly ash can therefore be used for different in-situ concrete applications based on the characteristic compressive strength at 28 days. It is recommended not to use these materials for reinforced concrete. Further research is required to assess the impact of using RSS on steel reinforcement.

- Precast units for external applications

Concrete mixes containing RSS and unprocessed fly ash can be used to manufacture different precast units for external applications. Precast units include, concrete kerbs, concrete paving flags, and external terrazzo tiles. Further standard tests are required to be performed before any large scale applications. The standard tests for the suggested precast units are described in BS EN 1340: 2003 (BSI, 2003c), BS EN 1339: 2003 (BSI, 2003b) and BS EN 13748-2: 2004 (BSI, 2004a).

- Self-compacting concrete

Self-compacting concrete containing RSS and unprocessed fly ash can be produced by either increasing RSS/Binder ratio or including workability additives, such as superplasticizer. Further research is required to assess the compliance of the suggested materials with the requirements of relevant standards.

- Cement-based materials for road construction

RSS and unprocessed fly ash together with Portland cement can be used to produce cement bound granular mixtures for roads, airfields and other trafficked areas. BS EN 14227-1:2013 (BSI, 2013b) specifies the requirements for their constituents, composition and laboratory performance classification. Further research is required to be undertaken on the suggested materials before any large scale applications.

10.3 LIMITATIONS

The limitations of the research programme were as follows:

1. The chemical composition of Raw Sewage Sludge (RSS) depends on a number of interacting factors including collection season, location of the treatment plant, retention time at the storage unit, and treatment processes that were applied to the source wastewater. The RSS sample that had been used throughout this research programme was obtained from a Sewage Treatment Works in the West Midlands in July 2011. It was advised by the treatment plant engineer that the RSS had been newly collected and pumped to the storage unit. It was also advised that no chemical additives, such as coagulants, were used during the treatment process.
2. The literature suggested that the inclusion of sewage sludge products prolongs both initial and final setting times of cement-based mixes. An attempt was therefore made to

evaluate the setting times of mortar mixes containing RSS. Unfortunately it was not possible to determine accurate readings as the presence of the suspended organics affected the performance of the setting time apparatus (Vicat Needle Apparatus).

3. As a health and safety measure and in order to minimise the risk of contamination, it was not permitted in the construction laboratories to cure concrete and mortar samples using water tanks. Alternatively, samples were cured using plastic and wrapping sheets.
4. For the mortar mixes with large proportions of unprocessed fly ash (Series 2), and the concrete mixes (Series 3), only one RSS/Binder ratio was used for each series (1 for Series 2, and 0.5 for Series 3). It would have been useful to investigate the influence varying RSS contents on tested properties.
5. It was not planned to carry out any micro-analytical work, such as x-ray differentiation (XRF), on the hydration products of cement-based materials containing RSS and unprocessed fly ash.
6. Sulphate attack was evaluated by measuring change in weight, compressive strength and visual observation of cubic samples. An attempt was made to observe the length change in mortar prisms submerged in sulphate solution by measuring the difference in length between two pairs of demec-studs attached to two sides of 40x40x160 mm in size prism. Unfortunately, the steel studs started to fall apart after a certain period of time and consequently no accurate readings were collected.
7. For the evaluation of leaching properties, it was not possible to determine the total concentration of each pollutant that was existed in the raw ingredients of each mix. The total concentration of each pollutant would have been compared with its corresponding concentration in the leachant and consequently the retention percentage would have been obtained.

10.4 FUTURE RECOMMENDATIONS

1. In the present study, mortar and concrete samples were cured by wrapping them with either plastic sheets or cling film. In order to strengthen the outcome of the investigation, other curing systems such as water curing and air curing need to be investigated.
2. The current study investigated the mechanical, durability and environmental properties of cement-based materials containing RSS and unprocessed fly ash. Although RSS sample was treated partially to eliminate hazardous pathogens, future work should assess the biological activities in both RSS and test specimens.
3. In the correlation chapter (Chapter 8) an attempt has been made to develop numerical functions to correlate the compressive strength with curing age and with one additional parameter including either RSS content, unprocessed fly ash content or sand content. In

order to develop a generic function that includes all the parameters above, a wider range of mortar mixes that contain different RSS content, unprocessed fly ash content and sand content need to be evaluated.

4. One sample of RSS was used throughout this study, which was collected in July 2011. More RSS samples need to be collected at different times throughout the year to evaluate the differences in the chemical composition and to study how this would influence the performance of investigated materials.
5. The present investigation focused on the evaluation of mortar mixes that contained RSS and unprocessed fly ash (Series 1). It also assessed a concrete series that consisted of five mixes (one cement:sand:gravel ratio, one RSS/Binder ratio and four percentages of unprocessed fly ash). A wider range of concrete mixes that contain various aggregate content, RSS/Binder ratios and unprocessed fly ash percentages need to be assessed to further strengthen the outcome of the study.
6. The inclusion of unprocessed fly ash significantly reduced the workability of tested mixes. In order to improve the mechanical properties, in particular the compressive strength, it is therefore suggested to use chemical admixtures, such as superplasticizer, to improve workability without the need of increasing RSS content.
7. Further research need to be undertaken to evaluate the acceptability of the use of cement-based materials containing RSS in the construction applications, and to highlight any social and cultural issues that might be of special importance to the society.
8. A further study is required to be undertaken to assess the impact of using RSS on steel reinforcement.

APPENDIX A: REFERENCES

AHMARUZZAMAN, M. 2010. A review on the utilization of fly ash. *Progress in Energy and Combustion Science,* 36**,** 327–363.

AL-MUFTI, R. L. & FRIED, A. N. 2012. The early age non-destructive testing of concrete made with recycled concrete aggregate. *Construction and Building Materials,* 37**,** 379–386.

AL-SUGAIR, F. H. 1995. Destructive and nondestructive tests for evaluating the strength properties of concrete containing silica fume. *Effect of curing conditions on the properties of OPS-concrete-Building and Environment, Pages 1167 - 1171.*

ALBANO, C., CAMACHO, N., HERNÁNDEZ, M., MATHEUS, A. & GUTIÉRREZ, A. 2009. Influence of content and particle size of waste pet bottles on concrete behavior at different w/c ratios. *Waste Management,* 29**,** 2707–2716.

ASTM 2008. ASTM C109/C109M-08: Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens).

ASTM 2009. ASTM D6316-09b: Standard test method for determination of total, combustible and carbonate carbon in solid residues from coal and coke.

ASTM 2012a. ASTM C150/C150M-12: Standard Specification for Portland Cement.

ASTM 2012b. ASTM C618-12a: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete.

ATICI, U. 2011. Prediction of the strength of mineral admixture concrete using multivariable regression analysis and an artificial neural network. *Expert Systems with Applications,* 38**,** 9609–9618.

ATIS, C. D. 2005. Strength properties of high-volume fly ash roller compacted and workable concrete, and influence of curing condition. *Cement and Concrete Research,* 35**,** 1112- 1121.

ATIS, C. D., KILIC, A. & SEVIM, U. K. 2004. Strength and shrinkage properties of mortar containing a nonstandard high-calcium fly ash. *Cement and Concrete Research,* 34**,** 99–102.

BAOJU, L., YOUJUN, X., SHIQIONG, Z. & QIANLIAN, Y. 2000. Influence of ultrafine fly ash composite on the fluidity and compressive strength of concrete. *Cement and Concrete Research,* 30**,** 1489-1493.

BENEZET, J.-C., ADAMIEC, P. & BENHASSAINE, A. 2008. Relation between silico-aluminous fly ash and its coal of origin. *Particuology,* 6**,** 85–92.

BLISSETT, R. S. & ROWSON, N. A. 2012. A review of the multi-component utilisation of coal fly ash. *Fuel,* 97**,** 1–23.

BOG, A. R. & TOPÇU, I. B. 2012. Influence of fly ash on corrosion resistance and chloride ion permeability of concrete. *Construction and Building Materials,* 31**,** 258–264.

BOUZOUBAA, N., ZHANG, M. H., BILODEAU, A. & MALHOTRA, V. M. 1998. Laboratory-produced high-volume fly ash blended cements: physical properties and compressive strength of mortars. *Cement and Concrete Research,* 28**,** 1555-1569.

BRINK, R. H. & HALSTEAD, W. J. 1956. Studies relating to the testing of fly ash for use in concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 51.*

BRITISH LIME ASSOCIATION. 2013. *Sewage sludge treatment* [Online]. Available: http://www.britishlime.org/technical/sewage_sludge_treatment.php [Accessed 05/03/2013.

BROWN, R. C. & DYKSTRA, J. 1995. Systematic errors in the use of loss-on-ignition to measure unburned carbon in fly ash. *Fuel,* 74**,** 570-574.

BSI 1986. BS 1881-125: Testing concrete -Part 125: Methods for mixing and sampling fresh concrete in the laboratory.

BSI 1996a. BS 3892-2: Pulverized-fuel ash-Specification for pulverized-fuel ash to be used as a Type I addition.

BSI 1996b. BS 4027: Specification for Sulfate-resisting Portland cement.

BSI 1996c. BS EN 933-2:Tests for geometrical properties of aggregates-Part 2: Determination of particle size distribution-Test sieves, nominal size of apertures.

BSI 1997. BS 3892-3:Pulverized-fuel ash-Specification for pulverized-fuel ash for use in cementitious grouts.

BSI 1998. BS EN 1097-3:Tests for mechanical and physical properties of aggregates-Part 3: Determination of loose bulk density and voids.

BSI 1999a. BS EN 1015-3: Methods of test for mortar for masonry -Part 3: Determination of consistence of fresh mortar (by flow table).

BSI 1999b. BS EN 1015-11: Methods of test for mortar for masonry-Part 11: Determination of flexural and compressive strength of hardened mortar.

BSI 2000a. BS EN 197-1: Cement-Part 1: Composition, specifications and conformity criteria for common cements.

BSI 2000b. BS EN 206-1: Concrete-Part 1: Specification, performance, production and conformity.

BSI 2000c. BS EN 1097-6: Tests for mechanical and physical properties of aggregates- Part 6: Determination of particle density and water absorption.

BSI 2002a. BS EN 1008: Mixing water for concrete-Specification for sampling, testing and assessing the suitability of water, including water recovered from processes in the concrete industry, as mixing water for concrete.

BSI 2002b. BS EN 12617-4: Products and systems for the protection and repair of concrete structures-Test methods-Part 4: Determination of shrinkage and expansion.

BSI 2002c. BS EN 13055-1: Lightweight aggregates. Lightweight aggregates for concrete, mortar and grout.

BSI 2002d. BS EN 13139: Aggregates for mortar.

BSI 2003a. BS EN 998-2: Specification for mortar for masonry-Part 2: Masonry mortar.

BSI 2003b. BS EN 1339: Concrete paving flags-Requirements and test methods.

BSI 2003c. BS EN 1340: Concrete kerb units-Requirements and test methods.

BSI 2004a. BS EN 13748-2: Terrazzo tiles-Part 2: Terrazzo tiles for external use.

BSI 2004b. BS EN 14227-3: Hydraulically bound mixtures-Specifications-Part 3: Fly ash bound mixtures.

BSI 2004c. BS EN 14227-4: Hydraulically bound mixtures-Specifications-Part 4: Fly ash for hydraulically bound mixtures.

BSI 2005. BS EN 196-1: Methods of testing cement-Part 1: Determination of strength.

BSI 2006. BS EN 14227-14: Hydraulically bound mixtures-Specifications-Part 14: Soil treated by fly ash.

BSI 2007a. BS EN 450-1:Fly ash for concrete-Part 1: Definition, specifications and conformity criteria.

BSI 2007b. BS EN 13242:2002+A1:2007: Aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction.

BSI 2008a. BS EN 12620:2002 +A1:2008: Aggregates for concrete.

BSI 2008b. Draft BS EN 15863: Characterization of waste-Leaching behaviour test for basic characterisation-Dynamic Monolithic Leaching Test with periodic leachant renewal under fixed test conditions.

BSI 2008c. PD CEN/TR 15697: Cement-Performance testing for sulfate resistance-State of the art report.

BSI 2008d. prEN 15863: Draft BS EN 15863 Characterization of waste-Leaching behaviour test for basic characterisation-Dynamic Monolithic Leaching Test with periodic leachant renewal under fixed test conditions.

BSI 2009a. BS EN 12350-2: Testing fresh concrete-Part 2: Slump test.

BSI 2009b. BS EN 12390-3: Testing hardened concrete-Part 3: Compressive strength of test specimens.

BSI 2009c. BS EN 12390-5: Testing hardened concrete Part 5: Flexural strength of test specimens.

BSI 2009d. BS EN 12390-7: Testing hardened concrete Part 7: Density of hardened concrete.

BSI 2009e. BS ISO1920-8: Testing of concrete-Part 8: Determination of drying shrinkage of concrete for samples prepared in the field or in the laboratory. .

BSI 2009f. BS ISO 1920-8: Testing of concrete-Part 8: Determination of drying shrinkage of concrete for samples prepared in the field or in the laboratory.

BSI 2010a. BS EN 459-1: Building lime-Part 1: Definitions, specifications and conformity criteria.

BSI 2010b. BS EN 998-2: Specification for mortar for masonry-Part 2: Masonry mortar.

BSI 2011a. BS EN 197-1: Cement-Part 1: Composition, specifications and conformity criteria for common cements.

BSI 2011b. BS EN 771-3: Specification for masonry units-Aggregate concrete masonry units (dense and lightweight aggregates).

BSI 2012a. BS 8500-1:2006+A1:2012: Concrete. Complementary British Standard to BS EN 206-1. Method of specifying and guidance for the specifier.

BSI 2012b. BS 8500-2: 2006+A1: 2012: Concrete-Complementary British Standard to BS EN 206-1-Part 2: Specification for constituent materials and concrete

BSI 2012c. BS EN 933-1: Tests for geometrical properties of aggregates-Part 1: Determination of particle size distribution-Sieving method.

BSI 2013a. BS EN 206: Concrete-Specification, performance, production and conformity.

BSI 2013b. BS EN 14227-1: Hydraulically bound mixtures-Specifications-Part 1: Cement bound granular mixtures.

BUTALIA, T. S., WOLFE, W. E. & LEE, J. W. 2001. Evaluation of a dry FGD material as a flowable fill. *Fuel,* 80**,** 845-850.

CAMILLERI, J., SAMMUT, M. & MONTESIN, F. E. 2006. Utilization of pulverized fuel ash in Malta. *Waste Management,* 26**,** 853–860.

CAO, C., SUN, W. & QIN, H. 2000. The analysis on strength and fly ash effect of roller-compacted concrete with high volume fly ash. *Cement and Concrete Research,* 30**,** 71-75.

CASTRO, J., BENTZ, D. & WEISS, J. 2011. Effect of sample conditioning on the water absorption of concrete. *Cement and Concrete Composites,* 33**,** 805–813.

CENTRAL ELECTRICITY GENERATING BOARD 1967. PFA data book. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 60.*

CHAU, C. K., CHAN, J. & LI, Z. 2009. Influences of fly ash on magnesium oxychloride mortar. *Cement and Concrete Composites,* 31**,** 250–254.

CHEESEMAN, C. R. & VIRDI, G. S. 2005. Properties and microstructure of lightweight aggregate produced from sintered sewage sludge ash. *Resources, Conservation and Recycling,* 45**,** 18–30.

CHEILAS, A., KATSIOTI, M., GEORGIADES, A., MALLIOU, O., TEAS, C. & HANIOTAKIS, E. 2007. Impact of hardening conditions on to stabilized/solidified products of cement–sewage sludge–jarosite/alunite. *Cement and Concrete Composites,* 29**,** 263-269.

CHEN, H.-J., HUANG, S.-S., TANG, C.-W., MALEK, M. A. & EAN, L.-W. 2012. Effect of curing environments on strength, porosity and chloride ingress resistance of blast furnace slag cement concretes: A construction site study. *Construction and Building Materials,* 35**,** 1063-1070.

CHEN, L. & LIN, D.-F. 2009a. Stabilization treatment of soft subgrade soil by sewage sludge ash and cement. *Journal of Hazardous Materials,* 162**,** 321-327.

CHEN, L. & LIN, D. F. 2009b. Applications of sewage sludge ash and nano-SiO2 to manufacture tile as construction material. *Construction and Building Materials,* 23**,** 3312-3320.

CHINDAPRASIRT, P., HOMWUTTIWONG, S. & SIRIVIVATNANON, V. 2004. Influence of fly ash fineness on strength, drying shrinkage and sulfate resistance of blended cement mortar. *Cement and Concrete Research,* 34**,** 1087–1092.

CHINDAPRASIRT, P., KANCHANDA, P., SATHONSAOWAPHAK, A. & CAO, H. T. 2007. Sulfate resistance of blended cements containing fly ash and rice husk ash. *Construction and Building Materials,* 21**,** 1356-1361.

CHINDAPRASIRT, P. & RUKZON, S. 2008. Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk ash and fly ash mortar. *Construction and Building Materials,* 22**,** 1601-1606.

CHIOU, I.-J., WANG, K.-S., CHEN, C.-H. & LIN, Y.-T. 2006. Lightweight aggregate made from sewage sludge and incinerated ash. *Waste Management,* 26**,** 1453-1461.

COMPTON, F. R. & MACNIS, C. 1952. Feild trial of fly ash concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 62.*

COPELAND, B. G. T. 1982. PFA concrete for hydraulic tunnels and shafts, Dinorwick pumped storage scheme-Case history. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 60.*

CUSIDÓ, J. A. & SORIANO, C. 2011. Valorization of pellets from municipal WWTP sludge in lightweight clay ceramics. *Waste Management,* 31**,** 1372-1380.

CYR, M., COUTAND, M. & CLASTRES, P. 2007. Technological and environmental behavior of sewage sludge ash (SSA) in cement-based materials. *Cement and Concrete Research,* 37**,** 1278-1289.

DAVIS, R. E., CARLSON, R. W., KELLY, J. W. & DAVIS, H. E. 1937. Properties of cement and concrete containing fly ash. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 46.*

DEFRA 2012. Waste water treatment in the United Kingdom-2012-Implementation of the European Union Urban Waste Water Treatment Directive-91/271/EEC.

DEHWAH, H. A. F. 2012. Mechanical properties of self-compacting concrete incorporating quarry dust powder, silica fume or fly ash. *Construction and Building Materials,* 26**,** 547–551.

DEMIRBOG, R., TURKMEN, I. B. & KARAKOC, M. B. 2004. Relationship between ultrasonic velocity and compressive strength for high-volume mineral-admixtured concrete. *Cement and Concrete Research,* 34**,** 2329–2336.

DHOLE, R. D., THOMAS, M. D. A., FOLLIARD, K. J. & DRIMALAS, T. 2009. Effect of fly ash composition on the sulfate resistance of concrete. *Annual Conference-Canadian Society for Civil Engineering Proceedings,* 3**,** 1549 - 1558.

DIAZ, E. I., ALLOUCHE, E. N. & EKLUND, S. 2010. Factors affecting the suitability of fly ash as source material for geopolymers. *Fuel,* 89**,** 992–996.

DIKEOU, J. T. 1970. Fly ash increases resistance of concrete to sulphate attack. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 171.*

DIONEX CORPORATION 2004. ICS-90: Ion chromatography system operator's manual. 4 ed.

DUNSTER, D. A. M. 2007. *Incinerated sewage sludge ash (ISSA) in autoclaved aerated concrete (AAC)* [Online]. Available: http://www.smartwaste.co.uk/filelibrary/Aeratedconcrete_Incinsewagesludgeash.pdf.

DUTTA, B. K., KHANRA, S. & MALLICK, D. 2009. Leaching of elements from coal fly ash: Assessment of its potential for use in filling abandoned coal mines. *Fuel,* 88**,** 1314–1323.

ELFERT, R. J. 1973. Bureau of reclamation experinces with fly ash and other pozzolans in concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 61.*

ESCALANTE-GARCíA, J. I. & SHARP, J. H. 2005. The microstructure and mechanical properties of blended cements hydrated at various temperatures. *Cement and Concrete Research,* 31**,** 695-702.

EUR-LEX. 2013. *Council Directive 80/68/EEC of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances* [Online]. Available: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31980L0068:EN:HTML [Accessed 25/12/2013 2013].

FAVONI, C., MINICHELLI, D., TUBARO, F., BRUCKNER, S., BACHIORRINI, A. & MASCHIO, S. 2005. Ceramic processing of municipal sewage sludge (MSS) and steelworks slags (SS). *Ceramics International,* 31**,** 697-702.

FERNANDES, V. A., PURNELL, P., STILL, G. T. & THOMAS, T. H. 2007. The effect of clay content in sands used for cementitious materials in developing countries. *Cement and Concrete Research,* 37**,** 751-758.

GARCÉS, P., PÉREZ CARRIÓN, M., GARCÍA-ALCOCEL, E., PAYÁ, J., MONZÓ, J. & BORRACHERO, M. V. 2008. Mechanical and physical properties of cement blended with sewage sludge ash. *Waste Management,* 28**,** 2495-2502.

GEBLER, S. H. & KLEIGER, P. 1986. Effect of fly ash on physical properties of concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 6, Page 77.*

GEOCHEMICAL INSTRUMENTATION AND ANALYSIS. 2013. *X-Ray Fluorescence (XRF)* [Online]. Available: http://serc.carleton.edu/research_education/geochemsheets/techniques/XRF.html [Accessed 09/04/13 2013].

GHOSH, A. & PRATT, P. L. 1981. Studies of the hydration reaction and microstructure of cement-fly ash paste. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 3, Page 20.*

GRAY, M. L., CHAMPAGNE, K. J., SOONG, Y., KILLMEYER, R. P., MAROTO-VALER, M. M., ANDRE´SEN, J. M., CIOCCO, M. V. & ZANDHUIS, P. H. 2002. Physical cleaning of high carbon fly ash. *Fuel Processing Technology,* 76**,** 11-21.

HAACH, V. G., VASCONCELOS, G. & LOURENÇO, P. B. 2011. Influence of aggregates grading and water/cement ratio in workability and hardened properties of mortars. *Construction and Building Materials,* 25**,** 2980-2987.

HAMLEY, P., LESTER, E., THOMPSON, A., CLOKE, M. & POLIAKOFF, M. 2001. The removal of carbon from fly ash using supercritical water oxidation. *International Ash Utilization Symposium***,** Page 85.

HANNESSON, G., KUDER, K., SHOGREN, R. & LEHMAN, D. 2012. The influence of high volume of fly ash and slag on the compressive strength of self-consolidating concrete. *Construction and Building Materials,* 30**,** 161–168.

HAQUE, M. N. & KAYALI, O. 1998. Properties of high-strength concrete using a fine fly ash. *Cement and Concrete Research,* 28**,** 1445–1452.

HARMANN, C. D. & MANGOTICH, E. 1987. A method for Predicting Sulfate Durability of Concrete. *ACI-Special Publication,* 100**,** 2135-2152.

HENKENSIEFKEN, R., CASTRO, J., BENTZ, D., NANTUNG, T. & WEISS, J. 2009. Water absorption in internally cured mortar made with water-filled lightweight aggregate. *Cement and Concrete Research,* 39**,** 883-892.

HER-YUNG, W. 2009. Durability of self-consolidating lightweight aggregate concrete using dredged silt. *Construction and Building Materials,* 23**,** 2332–2337.

HIGGINS, D. D. 2003. Increased sulfate resistance of ggbs concrete in the presence of carbonate. *Cement and Concrete Composites,* 25**,** 913-919.

HOVER, K. C. 2011. The influence of water on the performance of concrete. *Construction and Building Materials,* 25**,** 3003-3013.

HOWER, J. C., ROBERTSON, J. D., THOMAS, G. A., WANG, A. S., SCHRAM, W. H., GRAHAM, U. M., RATHBONE, R. F. & ROB1, T. L. 1996. Characterization of fly ash from Kentucky power plants. *Fuel,* 75**,** 403-411.

HURT, R. H. & GIBBINS, J. R. 1995. Residual carbon from pulverized coal fired boilers: 1. Size distribution and combustion reactivity. *Fuel,* 74**,** 471-480.

IZQUIERDO, M. & QUEROL, X. 2012. Leaching behaviour of elements from coal combustion fly ash: An overview. *International jornal of coal and geology,* 94**,** 54–66.

JALAL, M., FATHI, M. & FARZAD, M. 2013. Effects of fly ash and TiO 2 nanoparticles on rheological, mechanical, microstructural and thermal properties of high strength self compacting concrete. *Mechanics of Materials,* 61**,** 11-27.

JANKOWSKI, J., WARD, C. R., FRENCH, D. & GROVES, S. 2006. Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems. *Fuel,* 85**,** 243–256.

JIANLI, M., YOUCAI, Z., JINMEI, W. & LI, W. 2010. Effect of magnesium oxychloride cement on stabilization/solidification of sewage sludge. *Construction and Building Materials,* 24**,** 79-83.

JOHNSON, D. B. G. 1981. The use of fly ash in Cape Town RMC operations. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 60.*

JONES, M. R. & MCCARTHY, A. 2005. Utilising unprocessed low-lime coal fly ash in foamed concrete. *Fuel,* 84**,** 1398-1409.

JONES, R. & GATFIELD, E. N. 1955. Testing concrete by an ultrasonic puls technique. *In:* NEVILLE, A. M. & BROOKS, J. J. (eds.) *Concrete technology, Chapter 16, Page 232.*

JORDAN, M., ALMENDROCANDEL, M., ROMERO, M. & RINCON, J. 2005. Application of sewage sludge in the manufacturing of ceramic tile bodies. *Applied Clay Science,* 30**,** 219-224.

KATSIOTI, M., KATSIOTIS, N., ROUNI, G., BAKIRTZIS, D. & LOIZIDOU, M. 2008. The effect of bentonite/cement mortar for the stabilization/solidification of sewage sludge containing heavy metals. *Cement and Concrete Composites,* 30**,** 1013-1019.

KEARSLEY, E. P. & WAINWRIGHT, P. J. 2001. The effect of high fly ash content on the compressive strength of foamed concrete. *Cement and Concrete Research,* 31**,** 105-112.

KENAI, S., MENADI, B., ATTAR, A. & KHATIB, J. 2008. Effect of Crushed Limestone Fines on Strength of Mortar and Durability of Concrete. *International Conference on Construction and Building Technology, Conference A: Emerging technology in construction materials***,** 205-216.

KHATIB, J. M. 2005. Properties of concrete incorporating fine recycled aggregate. *Cement and Concrete Research,* 35**,** 763-769.

KHATIB, J. M. 2008a. Metakaolin concrete at a low water to binder ratio. *Construction and Building Materials,* 22**,** 1691-1700.

KHATIB, J. M. 2008b. Performance of self-compacting concrete containing fly ash. *Construction and Building Materials,* 22**,** 1963-1971.

KHATIB, J. M., MANGAT, P. S. & WRIGHT, L. 2006. Sulfate resistance of mortar containing simulated FGD waste. *Proceedings of the ICE - Construction Materials,* 159**,** 119-127.

KHATIB, J. M. & WILD, S. 1998. Sulphate resistance of metakaolin mortar. *Cement and Concrete Research,* 28**,** 83-92.

KIM, B. & PREZZI, M. 2008. Evaluation of the mechanical properties of class-F fly ash. *Waste Management,* 28**,** 649–659.

KOGBARA, R. B., AL-TABBAA, A., YI, Y. & STEGEMANN, J. A. 2013. Cement–fly ash stabilisation/solidification of contaminated soil: Performance properties and initiation of operating envelopes. *Applied Geochemistry,* 33**,** 64-75.

KOU, S.-C., POON, C.-S. & WAN, H.-W. 2012. Properties of concrete prepared with low-grade recycled aggregates. *Construction and Building Materials,* 36**,** 881-889.

KUTCHKO, B. G. & KIM, A. G. 2006. Fly ash characterization by SEM–EDS. *Fuel,* 85**,** 2537–2544.

LABCOMPARE. 2013. *Inductively Coupled Plasma Spectrometer (ICP AES / ICP OES)* [Online]. Available: http://www.labcompare.com/Spectroscopy/26-Inductively-Coupled-Plasma-Spectrometer-ICP-AES-ICP-OES/ [Accessed 08/04/13 2013].

LAM, C. S., POON, C. S. & CHAN, D. 2007. Enhancing the performance of pre-cast concrete blocks by incorporating waste glass-ASR consideration. *Cement and Concrete Composites,* 29**,** 616–625.

LAM, L., WONG, Y. L. & POON, C. S. 1998. Effect of fly ash and silica fume on compressive and fracture behaviors of concrete. *Cement and Concrete Research,* 28**,** 271–283.

LANE, R. O. & BEST, J. F. 1982. Properties of fly ash in portland cement concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 46.*

LIAN, C., ZHUGE, Y. & BEECHAM, S. 2011. The relationship between porosity and strength for porous concrete. *Construction and Building Materials,* 25**,** 4294-4298.

LIN, D.-F., LIN, K.-L., HUNG, M.-J. & LUO, H.-L. 2007. Sludge ash/hydrated lime on the geotechnical properties of soft soil. *Journal of Hazardous Materials,* 145**,** 58-64.

LIQIANG, Q. & YONGTAO, Y. 2011. Characteristics and the behavior in electrostatic precipitators of high-alumina coal fly ash from the Jungar power plant, Inner Mongolia, China. *Journal of Hazardous Materials,* 192**,** 222– 225.

LIU, G., ZHANG, H., GAO, L., ZHENG, L. & PENG, Z. 2004. Petrological and mineralogical characterizations and chemical composition of coal ashes from power plants in Yanzhou mining district, China. *Fuel Processing Technology,* 85**,** 1635– 1646.

LIU, Z., CHEN, Q., XIE, X., XUE, G., DU, F., NING, Q. & HUANG, L. 2011a. Utilization of the sludge derived from dyestuff-making wastewater coagulation for unfired bricks. *Construction and Building Materials,* 25**,** 1699-1706.

LIU, Z., ZHANG, Y., QIAN JIANG, G. S. & ZHANG, W. 2011b. In situ continuously monitoring the early age microstructure evolution of cementitious materials using ultrasonic measurement. *Construction and Building Materials,* 25**,** 3998–4005.

MAILVAGANAM, N. P., BHAGRATH, R. S. & SHAW, K. L. 1983. Effects of admixtures on portland cement concrete incorporating blast furnace slag and fly ash. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 46.*

MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. 1994. *Fly ash in concrete,* Canada, CANMET.

MALLIOU, O., KATSIOTI, M., GEORGIADIS, A. & KATSIRI, A. 2007. Properties of stabilized/solidified admixtures of cement and sewage sludge. *Cement and Concrete Composites,* 29**,** 55-61.

MALTAIS, Y., SAMSON, E. & MARCHAND, J. 2004. Predicting the durability of Portland cement systems in aggressive environments-laboratory validation. *Cement and Concrete Research,* 34**,** 1579-1589.

MANGAT, P. & KHATIB, J. 1995. Influence of fly ash, silica fume, and slag on sulfate resistance of concrete. *ACI Materials Journal,* 92**,** 542-552.

MANNAN, M. A., BASRI, H. B., ZAIN, M. F. M. & ISLAM, M. N. 2002. Effect of curing conditions on the properties of OPS-concrete. *Building and Environment,* 37**,** 1167 - 1171.

MANU, S., M.D, C. & J., O. 2003. Effect of Gypsum Formation on the Performance of Cement Mortar During External Sulfate Attack. *Cement and Concrete Research,* 33**,** 325-332.

MARTYS, N. S. & FERRARIS, C. E. 1997. Capillary transport in mortars and concrete. *Cement and Concrete Research,* 27**,** 747-760.

MEHTA, P. K. 1983. Mechanism of sulfate attack on portland cement concrete-Another look. *Cement and Concrete Research,* 13**,** 401-406.

MENADI, B., KENAI, S., KHATIB, J. & AıT-MOKHTAR, A. 2009. Strength and durability of concrete incorporating crushed limestone sand. *Construction and Building Materials,* 23**,** 625-633.

MERINO, I., ARÉVALO, L. F. & ROMERO, F. 2007. Preparation and characterization of ceramic products by thermal treatment of sewage sludge ashes mixed with different additives. *Waste Management,* 27**,** 1829-1844.

METCALF & EDDY, I., TCHOBANOGLOUS, G., STENSEL, H. D. & BURTON, F. L. 2003. *Wastewater engineering : treatment, disposal, reuse,* London, McGraw-Hill.

MINDESS, S., YOUNG, J. F. & DARWIN, D. 2003. *Concrete*, Prentice Hall.

MINERALS, V. 2014. *Portland Cement and Pozzolans-Custom-engineered, high performance, pozzolanic mineral additives for use in white cement, mortar, and concrete products* [Online]. Available: http://www.vitrominerals.com/?page_id=64 [Accessed 15/04/2014 2014].

MINNICK, L. J., WEBSTER, W. C. & PURDY, E. J. 1971. Predictions of the fly effect of fly ash in portland cement mortar and concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 51.*

MISHRAA, D. P. & DASB, S. K. 2010. Study of physico-chemical and mineralogical properties of Talcher coal fly ash for stowing in underground coal mines. *Materials Characterization,* 61**,** 1252-1259.

MO, K. H., YAP, K. K. Q., ALENGARAM, U. J. & JUMAAT, M. Z. 2014. The effect of steel fibres on the enhancement of flexural and compressive toughness and fracture characteristics of oil palm shell concrete. *Construction and Building Materials,* 55**,** 20-28.

MONTEIROA, P. J. M. & KURTISB, K. E. 2003. Time to failure for concrete exposed to severe sulfate attack. *Cement and Concrete Research,* 33**,** 987-993.

MONTERO, M. A., JORDÁN, M. M., HERNÁNDEZ-CRESPO, M. S. & SANFELIU, T. 2009. The use of sewage sludge and marble residues in the manufacture of ceramic tile bodies. *Applied Clay Science,* 46**,** 404-408.

MONZÓ, J., PAYÁ, J., BORRACHERO, M. V. & GIRBÉS, I. 2003. Reuse of sewage sludge ashes (SSA) in cement mixtures: the effect of SSA on the workability of cement mortars. *Waste Management,* 23**,** 373-381.

MONZÓ, J., PAYÁ, J., BORRACHERO, M. V. & PERIS-MORA, E. 1999. Mechanical behavior of mortars containing sewage sludge ash (SSA) and Portland cements with different tricalcium aluminate content. *Cement and Concrete Research,* 29**,** 87-94.

MOON, D. H., GRUBB, D. G. & REILLY, T. L. 2009. Stabilization/solidification of selenium-impacted soils using Portland cement and cement kiln dust. *Journal of Hazardous Materials,* 168**,** 944-951.

MORENO, N., QUEROL, X., ANDRE´S, J. M., STANTON, K., TOWLER, M., NUGTEREN, H., JANSSEN-JURKOVICOVA´D, M. & JONESE, R. 2005. Physico-chemical characteristics of European pulverized coal combustion fly ashes. *Fuel,* 84**,** 1351-1363.

MUN, K. 2007. Development and tests of lightweight aggregate using sewage sludge for nonstructural concrete. *Construction and Building Materials,* 21**,** 1583-1588.

N., A. 1989. Estabilitzacio´ /solidificacio´ de residus dcineracio´ de RSU en matrius de ciment. *In:* VALLS, S. & ZQUEZ, E. V. (eds.) *Leaching properties of stabilised/solidified cement-admixtures-sewage sludges systems, Pages 37-45.*

NAIK, T. R. & RAMME, B. W. 1990. Effect of high-calcium ash content on water demand, time of setting and compressive strength of concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 48.*

NAZARI, A. & RIAHI, S. 2011. The effects of SiO2 nanoparticles on physical and mechanical properties of high strength compacting concrete. *Composites,* B 42**,** 570-578.

NEMATZADEH, M. & NAGHIPOUR, M. 2012. Compressing fresh concrete technique and the effect of excess water content on physical–mechanical properties of compressed concrete. *Materials and Design,* 37**,** 256-267.

NEVILLE, A. M. & BROOKS, J. J. 2004. *Concrete technology-Revised edition-2001 standards update,* England, Pearson education limited.

OCEAN KING INDIA. 2013. *XRF Technology* [Online]. Available: http://www.oceankingindia.com/xrf.html [Accessed 09/04/13 2013].

OKOL, R. E. & BALAFOUTAS, G. 1998. Landfill sealing potentials of bottom ashes of sludge cakes. *Soil & Tillage Research,* 46**,** 307-314.

OWENS, P. L. 1979. Fly ash and its usage in concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Pages 50-51.*

PAN, S.-C., TSENG, D.-H., LEE, C.-C. & LEE, C. 2003a. Influence of the fineness of sewage sludge ash on the mortar properties. *Cement and Concrete Research,* 33**,** 1749-1754.

PAN, S., LIN, C. & TSENG, D. 2003b. Reusing sewage sludge ash as adsorbent for copper removal from wastewater. *Resources, Conservation and Recycling,* 39**,** 79-90.

PANYAKAPO, P. & PANYAKAPO, M. 2008. Reuse of thermosetting plastic waste for lightweight concrete. *Waste Management,* 28**,** 1581-1588.

PARK, Y. J., MOON, S. O. & HEO, J. 2002. Crystalline phase control of glass ceramics obtained from sewage sludge fly ash. *Ceramics International,* 29**,** 223-227.

PAYA, J., MONZO, J., BORRACHERO, M., AMAHJOUR, F. & PERIS-MORA, E. 2002. Loss on ignition and carbon content in pulverized fuel ashes (PFA): two crucial parameters for quality control. *Journal of chemical technology and biotechnology,* 77**,** 251-255.

PENN STATE UNIVERSITY. 2014. *Sulfate Attack-Proactive Avoidance* [Online]. Available: http://www.engr.psu.edu/ce/courses/ce584/concrete/library/chemical/sulfproact.html [Accessed 01/04/2014 2014].

PHILLEO, R. E. 1967. Fly ash in mass concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 61.*

POON, C. S., KOU, S. C. & LAM, L. 2006. Compressive strength, chloride diffusivity and pore structure of high performance metakaolin and silica fume concrete. *Construction and Building Materials,* 20**,** 858-865.

POON, C. S., LAM, L. & WONG, Y. L. 2000. A study on high strength concrete prepared with large volumes of low calcium fly ash. *Cement and Concrete Research,* 30**,** 447-455.

POON, C. S., QIAO, X. C. & LIN, Z. S. 2003. Pozzolanic properties of reject fly ash in blended cement pastes. *Cement and Concrete Research,* 33**,** 1857–1865.

PURDUE UNIVERSITY. 2013. *Scanning Electron Microscope* [Online]. Available: http://www.purdue.edu/rem/rs/sem.htm [Accessed 09/08/13 2013].

QI, Y., YUE, Q., HAN, S., YUE, M., GAO, B., YU, H. & SHAO, T. 2010. Preparation and mechanism of ultra-lightweight ceramics produced from sewage sludge. *Journal of Hazardous Materials,* 176**,** 76-84.

QIAN, G. R., SHIA, J., CAO, Y. L., XU, Y. F. & CHUI, P. C. 2008. Properties of MSW fly ash–calcium sulfoaluminate cement matrix and stabilization/solidification on heavy metals. *Journal of Hazardous Materials,* 152**,** 196-203.

RADOJEVIC, M. & BASHKIN, V. N. 1999. *Practical environmental analysis,* Cambridge, UK, The Royal Society of Chemistry.

RAHMANI, E., DEHESTANI, M., BEYGI, M. H. A., ALLAHYARI, H. & NIKBIN, I. M. 2013. On the mechanical properties of concrete containing waste PET particles. *Construction and Building Materials,* 47**,** 1302–1308.

RAMAKRISHNAN, V., COYLE, W. V., BROWN, J., TLUSTUS, A. & VENKATARAMANUJAM, P. 1981. Performance characteristics of concretes containing fly ash. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 48.*

RAMEZANIANPOUR, A. A. 1995. Effect of curing on the compressive strength, resistance to chloride-ion penetration and porosity of concretes incorporating slag, fly ash or silica fume. *Cement and Concrete Composites,* 17**,** 125-133.

REHSI, S. S. 1973. Studies on Indian fly ash and their use in structural concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 51.*

ROZIÈRE, E., LOUKILI, A., HACHEM, R. E. & GRONDIN, F. 2009. Durability of concrete exposed to leaching and external sulphate attacks. *Cement and Concrete Research,* 39**,** 1188–1198.

RUKZON, S. & CHINDAPRASIRT, P. 2012. Utilization of bagasse ash in high-strength concrete. *Materials and Design,* 34**,** 45-50.

SAMARAS, P., PAPADIMITRIOU, C. A., HARITOU, I. & ZOUBOULIS, A. I. 2008. Investigation of sewage sludge stabilization potential by the addition of fly ash and lime. *Journal of Hazardous Materials,* 154**,** 1052-1059.

SANTHANAM, M., COHEN, M. D. & OLEK, J. 2002. Modeling the effects of solution temperature and concentration during sulfate attack on cement mortars. *Cement and Concrete Research,* 32**,** 585–592.

SARKARA, A., RANOA, R., MISHRAB, K. K. & SINHAC, I. N. 2005. Particle size distribution profile of some Indian fly ash-a comparative study to assess their possible uses. *Fuel Processing Technology,* 86**,** 1221– 1238.

SEAR, L. K. A. 2011. Future trends for PFA in cementitious systems. *1st Future Cement Conference and Exhibition 2011-London Chamber of Commerce and Industry, London UK*.

SEBOK, T., SIMONıK, J. & KULıSEK, K. 2001. The compressive strength of samples containing fly ash with high content of calcium sulfate and calcium oxide. *Cement and Concrete Research,* 31**,** 1101-1107.

SHAFIGH, P., JUMAAT, M. Z., MAHMUD, H. B. & HAMID, N. A. A. 2012. Lightweight concrete made from crushed oil palm shell: Tensile strength and effect of initial curing on compressive strength. *Construction and Building Materials,* 27**,** 252-258.

SHI, C. & FERNANDEZ-JIMENEZ, A. 2006. Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements. *Journal of Hazardous Materials,* B137**,** 1656-1663.

SIDDIQUE, R. 2003. Effect of fine aggregate replacement with Class F fly ash on the mechanical properties of concrete. *Cement and Concrete Research,* 33**,** 539-547.

SIDDIQUE, R., KHATIB, J., YÜKSEL, I. & AGGARWAL, P. 2008. Strength properties of high-volume fly ash (HVFA) concrete incorporating steel fibres. *Excellence in Concrete Construction through Innovation: Proceedings of the conference***,** 149-154.

SINGH, M. & SIDDIQUE, R. 2013. Effect of coal bottom ash as partial replacement of sand on properties of concrete. *Resources, Conservation and Recycling,* 72**,** 20-32.

SINGH, T. S. & PANT, K. K. 2006. Solidification/stabilization of arsenic containing solid wastes using portland cement, fly ash and polymeric materials. *Journal of Hazardous Materials,* B131**,** 29-36.

SNELSON, D. G. & KINUTHIA, J. M. 2010a. Characterisation of an unprocessed landfill ash for application in concrete. *Journal of Environmental Management,* 91**,** 2117-2125.

SNELSON, D. G. & KINUTHIA, J. M. 2010b. Resistance of mortar containing unprocessed pulverised fuel ash (PFA) to sulphate attack. *Cement and Concrete Composites,* 32**,** 523-531.

SPECTRO. 2013. *XRF Spectrometers* [Online]. Available: http://www.spectro.com/pages/e/p0105.htm [Accessed 09/04/13 2013].

SPRAGG, R. P., CASTRO, J., LI, W., POUR-GHAZ, M., HUANG, P.-T. & WEISS, J. 2011. Wetting and drying of concrete using aqueous solutions containing deicing salts. *Cement and Concrete Composites,* 33**,** 535-542.

SU, N. & MIAO, B. 2003. A new method for the mix design of medium strength flowing concrete with low cement content. *Cement and Concrete Composites,* 25**,** 215–222.

SUA-IAM, G. & MAKUL, N. 2013. Utilization of limestone powder to improve the properties of self-compacting concrete incorporating high volumes of untreated rice husk ash as fine aggregate. *Construction and Building Materials,* 38**,** 455-464.

SUMER, M. 2012. Compressive strength and sulfate resistance properties of concretes containing Class F and Class C fly ashes. *Construction and Building Materials,* 34**,** 531–536.

TERMKHAJORNKIT, P., NAWA, T. & KURUMISAWA, K. 2006. Effect of water curing conditions on the hydration degree and compressive strengths of fly ash–cement paste. *Cement and Concrete Composites,* 28**,** 781–789.

THE BALTIC UNIVERSITY. 2013. *Chapter 12: Metal Flows and Environmental Impact* [Online]. Available: http://www.balticuniv.uu.se/environmentalscience/ch12/chapter12_g.htm [Accessed 08/04/13 2013].

THEODORATOS, P., MOIROU, A., XENIDIS, A. & PASPALIARIS, I. 2000. The use of municipal sewage sludge for the stabilization of soil contaminated by mining activities. *Journal of Hazardous Materials,* B77**,** 177-191.

TIAN, B. & COHEN, M. D. 2000. Does gypsum formation during sulfate attack on concrete lead to expansion? *Cement and Concrete Research,* 30**,** 117–123.

TIKALSKY, P. J., CARRASQUILLO, P. M. & CARRASQUILLO, R. L. 1988. Strength and durability consideration affecting mix propotioning of concrete containing fly ash. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 6, Page 78.*

TIKALSKY, P. J. & CARRASQUILLO, R. L. 1989. Influence of Fly Ash on the Sulfate Resistance of Concrete. *ACI-Materials Journal,* 89**,** 69-75.

TOMECZEK, J. & PALUGNIOK, H. 2002. Kinetics of mineral matter transformation during coal combustion. *Fuel,* 81**,** 1251–1258.

TOPCU, I. B. & CANBAZ, M. 2007. Effect of different fibers on the mechanical properties of concrete containing fly ash. *Construction and Building Materials,* 21**,** 1486–1491.

TORII, K., TANIGUCHI, K. & KAWAMURA, M. 1995. Sulfate resistance of high fly ash content concrete. *Cement and Concrete Research,* 25**,** 759–768.

UCHIKAWA, H. 1986. Effect of blending components on hydration and structure formation. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 3, Page 20.*

UKQAA. 2011. *Pulverised Fuel Ash, Gypsum, Cenospheres, Furnace Bottom Ash Provisional Utilisation Data for 2011 – Public Domain Version* [Online]. Available: http://www.ukqaa.org.uk/index_htm_files/2011_Utilisation_Public_version.pdf [Accessed 15/04/13 2013].

UKQAA. 2013a. *Technical datasheet 1-Fly Ash for concrete* [Online]. Available: http://www.ukqaa.org.uk/index_htm_files/Datasheet_1-0_Jul_2011.pdf [Accessed 21/04/13 2013].

UKQAA. 2013b. *Technical datasheet 1.6: The use of Fly Ash for reducing the heat of hydration* [Online]. Available: http://www.ukqaa.org.uk/index_htm_files/Datasheet_1-6_August_2011.pdf [Accessed 23/04/13 2013].

UKQAA. 2013c. *Technical Datasheet 2-Pulverised fuel ash for fill applications* [Online]. Available: http://www.ukqaa.org.uk/index_htm_files/Datasheet_2-0_May_2007.pdf [Accessed 21/04/13 2013].

UKQAA. 2013d. *Technical Datasheet 4-Lightweight aggregates manufactured from Pulverised Fuel ash* [Online]. Available: http://www.ukqaa.org.uk/index_htm_files/Datasheet_4-0_Jan_2003.PDF [Accessed 21/04/13 2013].

UKQAA. 2013e. *Technical Datasheet 6: Fly Ash in Pavement Construction-Overview of Fly Ash Bound Mixtures (FABM) & soil treated with fly ash (SFA)* [Online]. Available: http://www.ukqaa.org.uk/index_htm_files/Datasheet_6-0_Highway_Construction_May_2011.pdf [Accessed 21/04/13 2013].

UKQAA. 2013f. *Technical Datasheet 7: Furnace Bottom Ash (FBA) in Light Weight Aggregate (LWA) concrete blocks* [Online]. Available: http://www.ukqaa.org.uk/index_htm_files/Datasheet_7-0_Aug_2004.pdf [Accessed 21/04/13 2013].

UKQAA. 2013g. *Technical information for a wide range of applications for ash* [Online]. Available: http://www.ukqaa.org.uk/technical%20datasheets.htm [Accessed 21/04/13 2013].

UYGUNOGLU, T., TOPCU, I. B., GENCEL, O. & BROSTOW, W. 2012. The effect of fly ash content and types of aggregates on the properties of pre-fabricated concrete interlocking blocks (PCIBs). *Construction and Building Materials,* 30**,** 180–187.

UYSAL, M. & YILMAZ, K. 2011. Effect of mineral admixtures on properties of self-compacting concrete. *Cement and Concrete Composites,* 33**,** 771-776.

VALLS, S. 2000. Stabilisation and solidification of sewage sludges with Portland cement. *Cement and Concrete Research,* 30**,** 1671-1678.

VALLS, S. 2002. Leaching properties of stabilised/solidified cement-admixtures-sewage sludges systems. *Waste Management,* 22**,** 37–45.

VALLS, S., YAGÜE, A., VÁZQUEZ, E. & MARISCAL, C. 2004. Physical and mechanical properties of concrete with added dry sludge from a sewage treatment plant. *Cement and Concrete Research,* 34**,** 2203-2208.

VASSILEV, S. V. & VASSILEV, C. G. 2007. A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behaviour. *Fuel,* 86**,** 1490–1512.

VERANTH, J. M., PERSHING, D. W., SAROFIM, A. F. & SHIELD, J. E. 1998. Sources of unburned carbon in the fly ash produced from low-NOx pulverized coal combustion. *Twenty-Seventh Symposium (International) on Combustion***,** 1737-1744.

VOGLAR, G. E. & LESTAN, D. 2010. Solidification/stabilisation of metals contaminated industrial soil from former Zn smelter in Celje, Slovenia, using cement as a hydraulic binder. *Journal of Hazardous Materials,* 178**,** 926-933.

WANG, K., CHIOU, I., CHEN, C. & WANG, D. 2005. Lightweight properties and pore structure of foamed material made from sewage sludge ash. *Construction and Building Materials,* 19**,** 627-633.

WANG, X., JIN, Y., WANG, Z., NIE, Y., HUANG, Q. & WANG, Q. 2009. Development of lightweight aggregate from dry sewage sludge and coal ash. *Waste Management,* 29**,** 1330-1335.

WASTE ON LINE. 2010. *Sewage Sludge* [Online]. Available: http://www.wasteonline.org.uk/resources/Wasteguide/mn_wastetypes_sewagesludge.html/ [Accessed 12/11/2010.

WELSH, G. B. & BURTON, J. R. 1958. Sydney fly ash in concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 51.*

WHITEHURST, E. A. 1951. Soniscope Tests Concrete Structures. *Journal Proceedings,* 47**,** 433-444.

WILD, S., SABIR, B. B. & KHATIB, J. M. 1995. Factors influencing strength development of concrete containing silica fume. *Cement and Concrete Research,* 25**,** 1567-1580.

WILLIAMS, J. T. & OWENS, P. L. 1982. The implecations of a selected grade of United Kingdom pulverised fuel ash on the engineering design and use in structural concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 5, Page 63.*

WU, S., CHEN, X. & ZHOU, J. 2012. Influence of strain rate and water content on mechanical behavior of dam concrete. *Construction and Building Materials,* 36**,** 448–457.

YAGÜE, A., VALLS, S., VÁZQUEZ, E. & ALBAREDA, F. 2005. Durability of concrete with addition of dry sludge from waste water treatment plants. *Cement and Concrete Research,* 35**,** 1064-1073.

YANA, L., WANGA, Y., MAB, H., HANA, Z., ZHANGA, Q. & CHENB, Y. 2012. Feasibility of fly ash-based composite coagulant for coal washing wastewater treatment. *Journal of Hazardous Materials,* 203– 204**,** 221– 228.

YAP, S. P., ALENGARAM, U. J. & JUMAAT, M. Z. 2013. Enhancement of mechanical properties inpolypropylene–and nylon–fibre reinforced oil palm shell concrete. *Materials and Design,* 49**,** 1034–1041.

YAZICI, H., AYDIN, S., YIĞITER, H. & BARADAN, B. 2005. Effect of steam curing on class C high-volume fly ash concrete mixtures. *Cement and Concrete Research,* 35**,** 1122–1127.

YIN, C. Y., ALI, W. S. W. & LIM, Y. P. 2008. Oil palm ash as partial replacement of cement for solidification/ stabilization of nickel hydroxide sludge. *Journal of Hazardous Materials,* 150**,** 413-418.

YUAN, R. L. & COOK, J. E. 1983. Study of class C fly ash concrete. *In:* MALHOTRA, V. M. & RAMEZANIANPOUR, A. A. (eds.) *Fly ash in concrete, Chapter 6, Page 75.*

ZENTAR, R., WANG, D., ABRIAK, N. E., BENZERZOUR, M. & CHEN, W. 2012. Utilization of siliceous–aluminous fly ash and cement for solidification of marine sediments. *Construction and Building Materials,* 35**,** 856-863.

ZHANG, W., ZAKARIA, M. & HAMA, Y. 2013. Influence of aggregate materials characteristics on the drying shrinkage properties of mortar and concrete. *Construction and Building Materials,* 49**,** 500-510.

ZHANG, X.-Y., QI-CHAOWANG, ZHANG, S.-Q., SUN, X.-J. & ZHANG, Z.-S. 2009. Stabilization/solidification (S/S) of mercury-contaminated hazardous wastes using thiol-functionalized zeolite and Portland cement. *Journal of Hazardous Materials,* 168**,** 1575-1580.

ZHAO, Y., YUE, Q., LI, R., YUE, M., HAN, S., GAO, B., LI, Q. & YU, H. 2009. Research on sludge-fly ash ceramic particles (SFCP) for synthetic and municipal wastewater treatment in biological aerated filter (BAF). *Bioresource Technology,* 100**,** 4955-4962.

APPENDIX B: EU WATER QUALITY PARAMETERS (EPA-IRELAND, 2001).

Element/Ion	Unit	Surface Water Regulations [1989]			Drinking Water Directive [98/83/EC]	Ground Water Directive [80/68/EEC]	Occurrence/Origin****
		A1 Waters*	A2 Waters*	A3 Waters*			
Aluminium (Al)	mg/l Al	-	-	-	200	-	*Aluminium is one of the most abundant elements in the earth's crust. A salt, aluminium sulphate, is very widely used for colour- and colloid-removal in the treatment of waters for drinking.*
Iron (Fe)	mg/l Fe	0.2	2	2	0.2	-	*Geological formations (especially under reducing conditions); acid drainage; effluent discharges.*
Cobalt (Co)	mg/l Co	-	-	-	-	List II substance***	*Occurs in ores. Presence in water due to discharges.*
Nickel (Ni)	mg/l Ni	-	-	-	0.02	List II substance***	*Principal sources are minerals and industrial wastes.*
Copper (Cu)	mg/l Cu	0.05	0.1	1	2	List II substance***	*Ores; industrial wastes.*
Zink (Zn)	mg/l Zn	3	5	5	-	-	*Natural geological occurrence and from wastes.*
Mercury (Hg)	mg/l Hg	0.001	0.001	0.001	0.001	List I substance**	*Normally from industrial waste discharges.*
Manganese (Mn)	mg/l Mn	0.05	0.3	1	0.05	-	*Widely distributed constituent of ores and rocks*
Cadmium (Cd)	mg/l Cd	0.005	0.005	0.005	0.005	List I substance**	*In ores, including those of zinc. Cadmium in water is due nearly exclusively to industrial discharges (e.g. from electroplating, paint making, manufacture of plastics etc) and landfill leachates.*
Barium (Ba)	mg/l Ba	0.1	1	1	-	List II substance***	*Naturally occurring mineral (e.g. in barytes), which has in the past been mined in several places in Ireland, including Benbulben in County Sligo. According to the WHO Guidelines, while food is the main source of barium intake by humans, where barium occurs in drinking water supplies the latter can contribute a significant proportion of total intake.*
Selenium (Se)	mg/l Se	0.01	0.01	0.01	0.01	List II substance***	*Weathering of rocks/soils, but major environmental sources are man-made.*
Arsenic (As)	mg/l As	0.05	0.05	0.1	0.01	List II substance***	*This element is very widely distributed throughout the earth's crust, according to the WHO Guidelines, which state that "it is introduced into water through the dissolution of minerals and ores, from industrial effluents, and from atmospheric deposition: concentrations in ground water in some areas are sometimes elevated as a result of erosion from natural sources. The average daily intake of inorganic arsenic in water is estimated to be similar to that from food; intake from air is negligible." Arsenic is used in the glass and semiconductor industries and as a fungicide in timber processing. A major US emission source is coal-fired power plant.*
Molybdenum (Mo)	mg/l Mo	-	-	-	-	List II substance***	*Natural molybdenum levels in waters likely to be used as sources of public supply are very low and, in any event, human toxicity caused by this metal is very rare. However, the sensitivity of livestock to the element has been found to be significant although no specific limits for water have apparently been set for animal drinking water*
Chromium (Cr)	mg/l Cr	0.05	0.05	0.05	0.05	List II substance***	*Natural occurrence is in ore, but chromium arises in surface waters from discharges from electroplating, tanning, textile, paint and dyeing plants.*
Lead (Pb)	mg/l Pb	0.05	0.05	0.05	0.01	List II substance***	*Leaching from ores; effluent discharges; attack on water pipes.*
Tin (Sn)	mg/l Sn	-	-	-	-	List II substance***	*Ores, effluents from tin-plating and alloy manufacture.*
Bromide		-	-	-	-	-	
Chloride (C^{l-})	mg/l C^{l-}	250	250	250	-	-	*Chloride exists in all natural waters, the concentrations varying very widely and reaching a maximum in sea water (up to 35,000 mg/l Cl). In fresh waters the sources include soil and rock formations, sea spray and waste discharges. Sewage contains large amounts of chloride, as do some industrial effluents.*
Fluoride (F^-)	mg/l F^-	1	1.7	1.7	1.5	List II substance***	*Occurs naturally in quite rare instances; arises almost exclusively from fluoridation of public water supplies and from industrial discharges.*
Nitrite (NO_2^-)	mg/l NO_2^-	-	-	-	0.5	List II substance***	*Generally from untreated or partially treated wastes.*
Nitrate (NO_3^-)	mg/l NO_3^-	50	50	50	50	-	*Oxidation of ammonia: agricultural fertiliser runs off.*
Phosphate (PO_4^{3-})	mg/l PO_4^{3-}	0.5	0.7	0.7	-	List II substance***	*Phosphorus occurs widely in nature in plants, in micro-organisms, in animal wastes and so on. It is widely used as an agricultural fertiliser and as a major constituent of detergents, particularly those for domestic use. Run-off and sewage discharges are thus important contributors of phosphorus to surface waters.*
Sulphate (SO_4^{2-})	mg/1 SO_4^{2-}	200	200	200	250	-	*Rocks, geological formations, discharge and so on.*

Notes:

* *EU Council Directive 75/440/EEC categorises surface water into Category A1: Simple physical treatment and disinfection, e. g. rapid filtration and disinfection, Category A2: Normal physical treatment, chemical treatment and disinfection, e.g. pre-chlorination, coagulation, flocculation, decantation, filtration, disinfection (final chlorination), and Category A3: Intensive physical and chemical treatment, extended treatment and disinfection e.g. chlorination to break-point, coagulation, flocculation, decantation, filtration, adsorption (activated carbon), disinfection (ozone, final chlorination)* (EUR-Lex, 2013a).

** *List I contains the individual substances which belong to the families and groups of substances enumerated below, with the exception of those which are considered inappropriate to list I on the basis of a low risk of toxicity, persistence and bioaccumulation. List I includes the followings; Organohalogen compounds and substances which may form such compounds in the aquatic environment, Organophosphorus compounds, Organotin compounds, Substances which possess carcinogenic mutagenic or teratogenic properties in or via the aquatic environment, Mercury and its compounds, Cadmium and its compounds, Mineral oils and hydrocarbons and Cyanides* (EUR-Lex, 2013b).

*** *List II contains the individual substances and the categories of substances belonging to the families and groups of substances listed below which could have a harmful effect on groundwater;*
1. The following metalloids and metals and their compounds: Zinc, Copper, Nickel, Chrome, Lead, Selenium, Arsenic, Antimony, Molybdenum, Titanium, Tin, Barium, Beryllium, Boron, Uranium, Vanadium, Cobalt, Thallium, Tellurium Silver.
2. Biocides and their derivatives not appearing in list I.
3. Substances which have a deleterious effect on the taste and/or odour of groundwater, and compounds liable to cause the formation of such substances in such water and to render it unfit for human consumption.
4. Toxic or persistent organic compounds of silicon, and substances which may cause the formation of such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances.
5. Inorganic compounds of phosphorus and elemental phosphorus.
6. Fluorides.
7. Ammonia and nitrites. Where certain substances in list II are carcinogenic, mutagenic or teratogenic, they are included in category 4 of this list (EUR-Lex, 2013b).

**** Source: (EPA-Ireland, 2001)

References:

EPA-IRELAND 2001. *PARAMETERS OF WATER QUALITY: Interpretation and Standards*, the Environmental Protection Agency, Ireland.

EUR-LEX. 2013a. *Council Directive 75/440/EEC of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States* [Online]. Available: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31975L0440:EN:HTML [Accessed 25/12/2013].

EUR-LEX. 2013b. *Council Directive 80/68/EEC of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances* [Online]. Available: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31980L0068:EN:HTML [Accessed 25/12/2013].

APPENDIX C: FURTHER CORRELATION

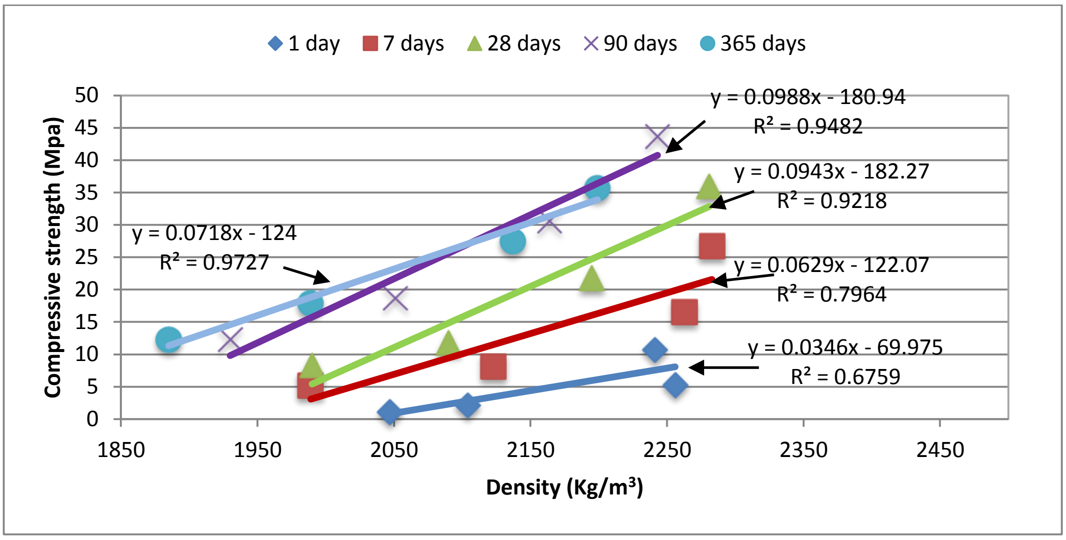


Figure ApxC.1: The relationship between compressive strength and density for mortar mixes with different RSS/Cement ratios (Group 1).

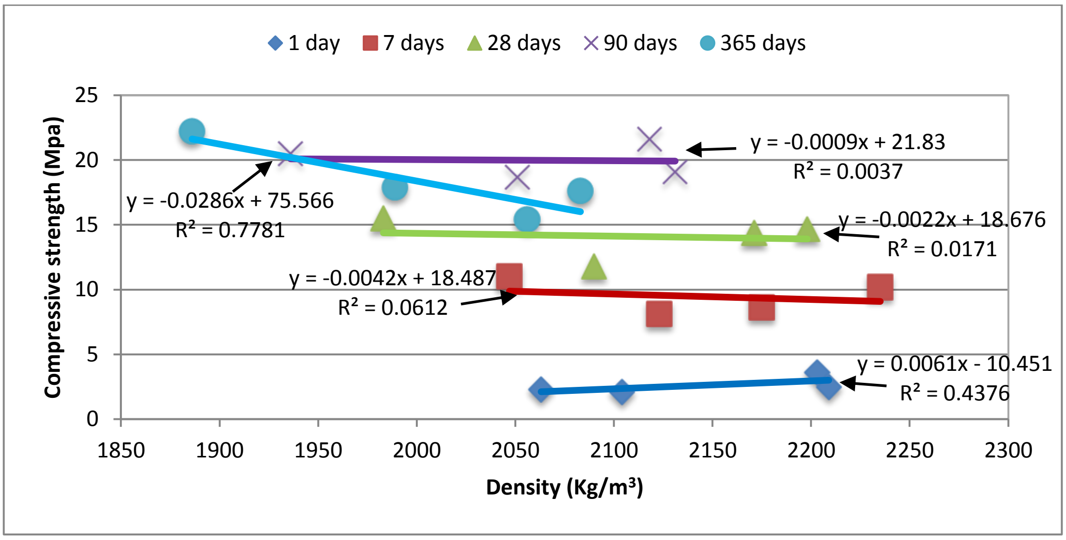


Figure ApxC.2: The relationship between compressive strength and density of mortar mixes with different sand content (Group 2).

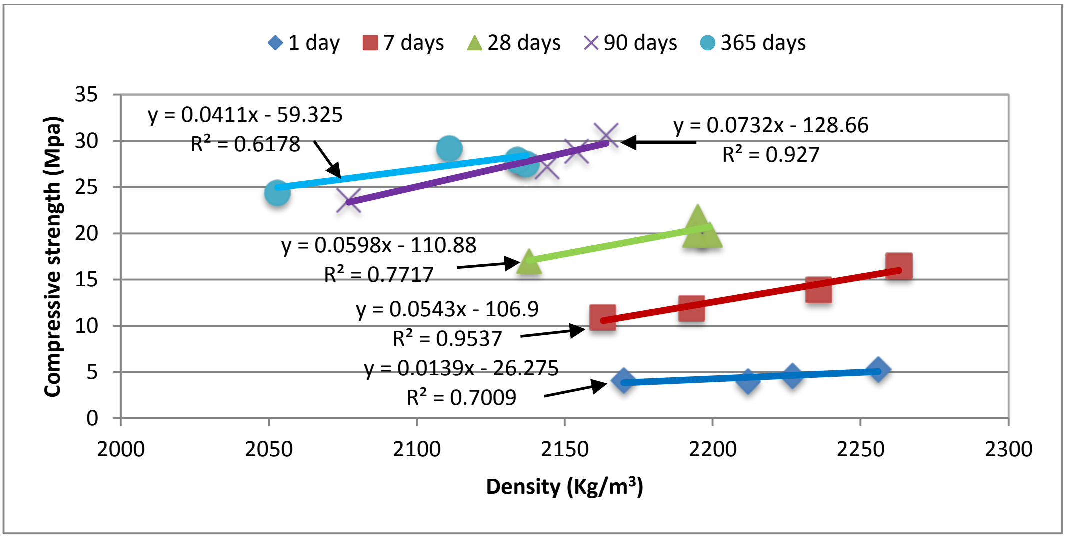


Figure ApxC.3: The relationship between compressive strength and density of mortar mixes with different fly ash content and RSS/Binder ratio of 0.65 (Group 3).

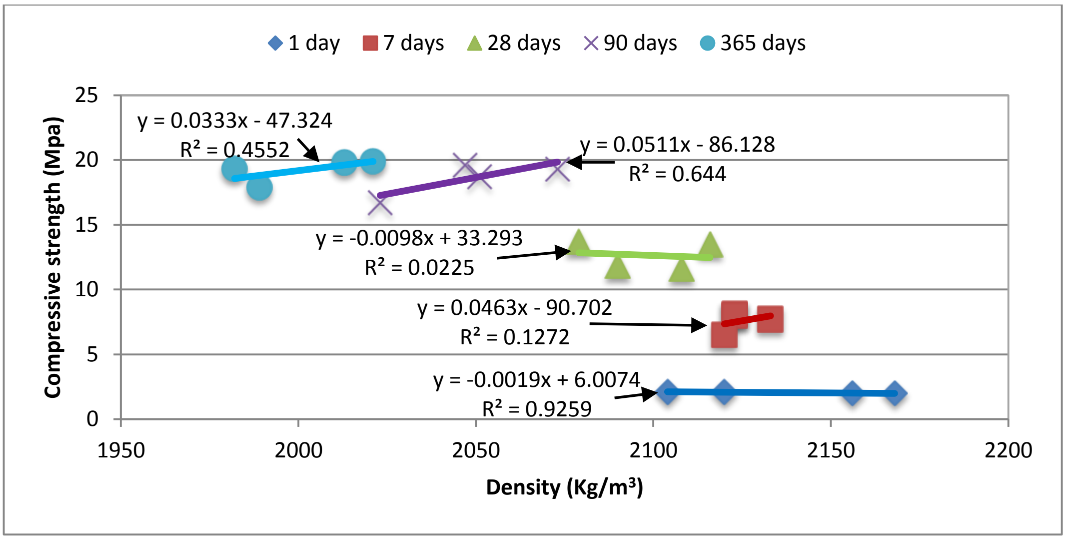


Figure ApxC.4: The relationship between compressive strength and density of mortar mixes with different fly ash content and RSS/Binder ratio of 0.8 (Group 4).

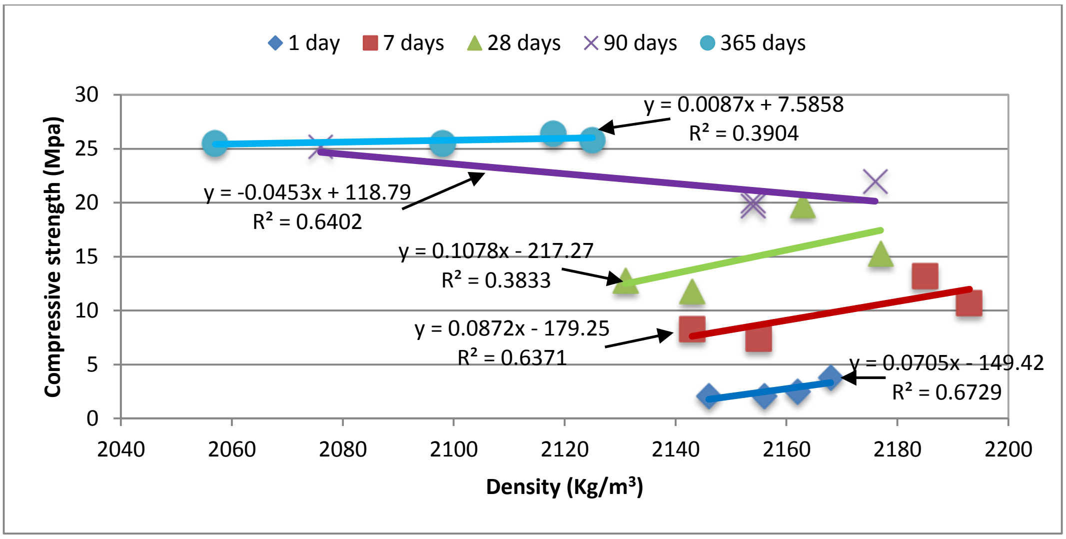


Figure ApxC.5: The relationship between compressive strength and density of the control mixes with different fly ash content and Water/Binder ratio of 0.8 (Group 5).

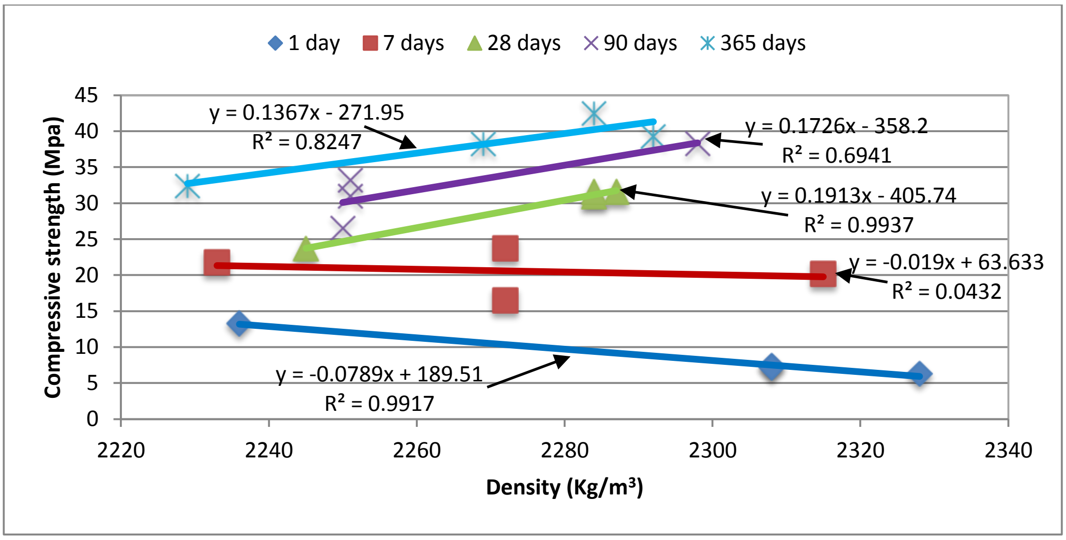
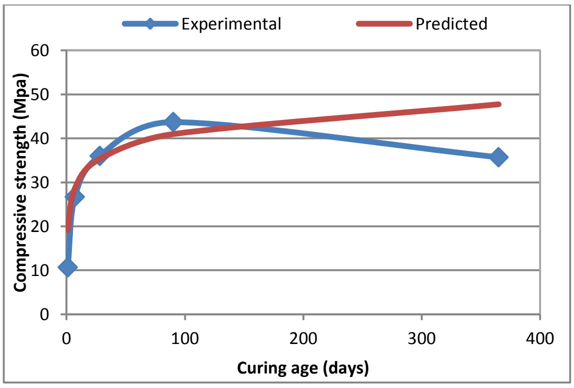
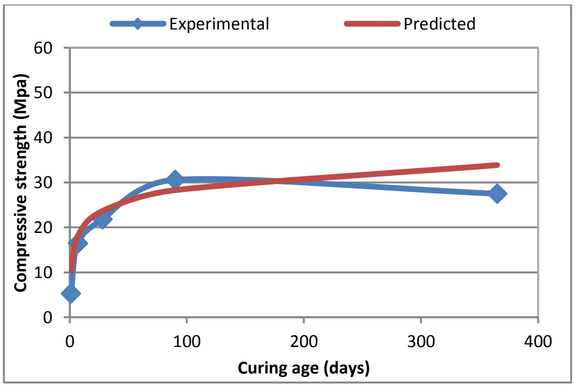


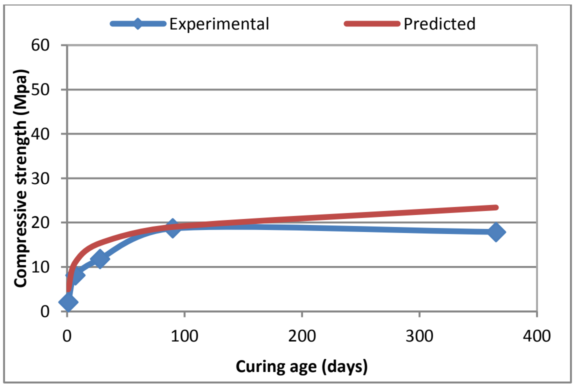
Figure ApxC.6: The relationship between compressive strength and density of the concrete mixes (Series 3).



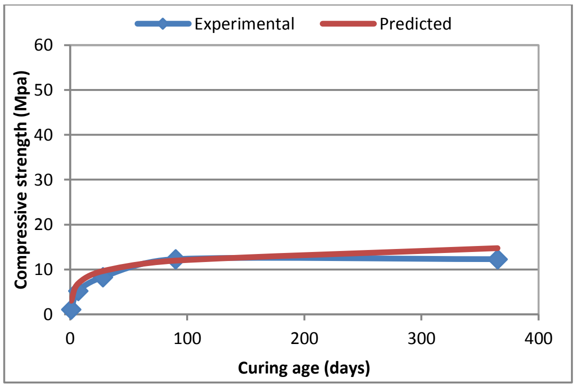
a: RSS/Cement ratio=0.5



B: RSS/Cement ratio =0.65

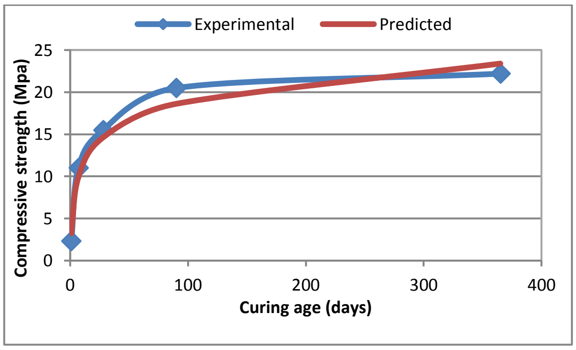


C: RSS/Cement ratio =0.8

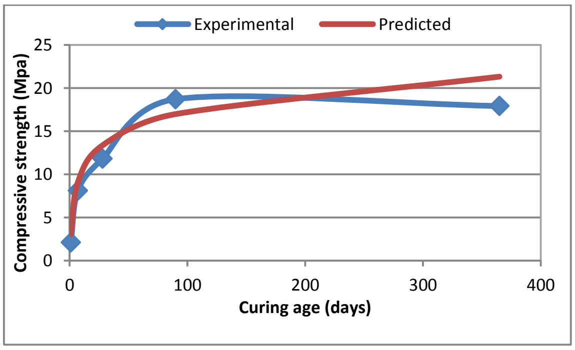


D: RSS/Cement ratio =1

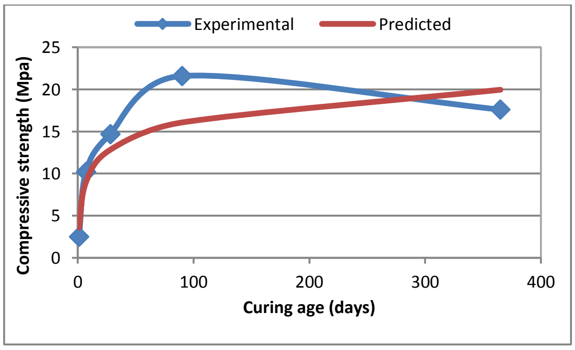
Figure ApxC.7: Experimental and predicted compressive strength for mortar mixes with different RSS/Cement ratios (Equation 8.1).



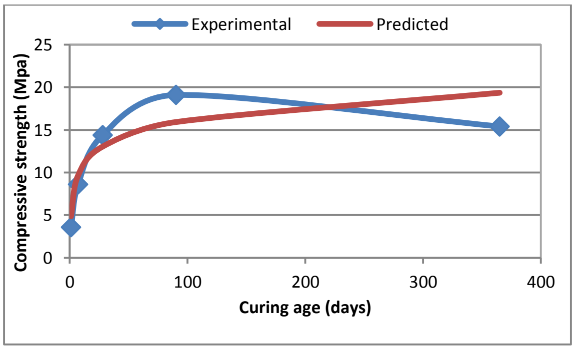
A: Sand:Cement ratio=3



B: Sand:Cement ratio=4.5

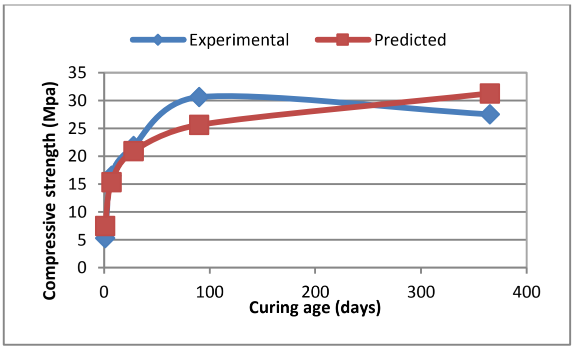


C: Sand:Cement ratio=6

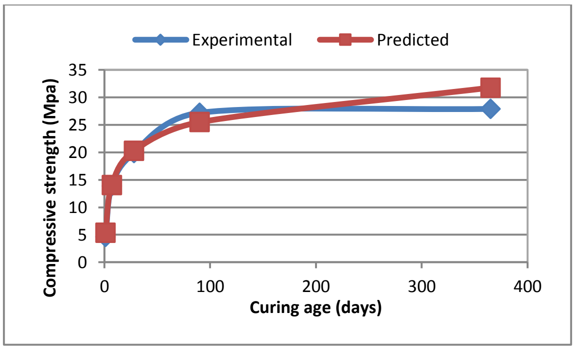


D: Sand:Cement ratio=7.5

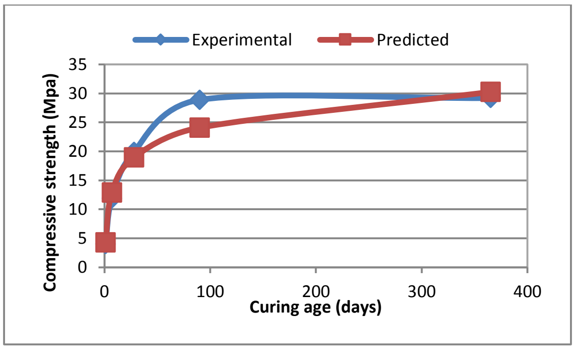
Figure ApxC.8: Experimental and predicted compressive strength for mortar mixes with different Sand content (Equation 8.2).



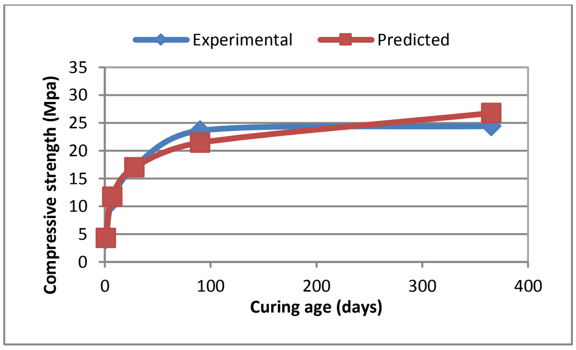
A: Fly ash content =0%



B: Fly ash content =10%

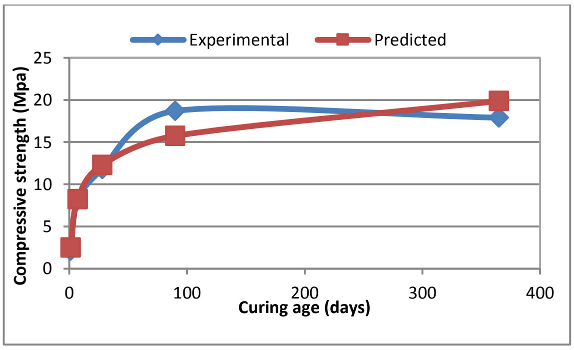


C: Fly ash content =20%

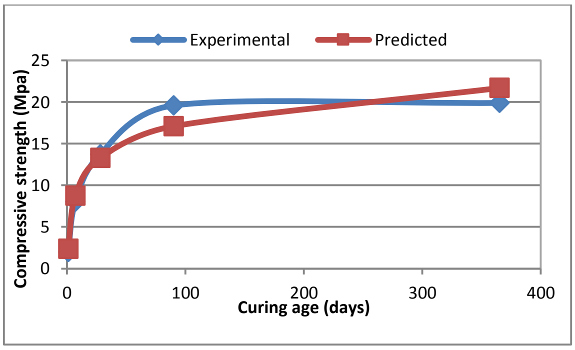


D: Fly ash content =30%

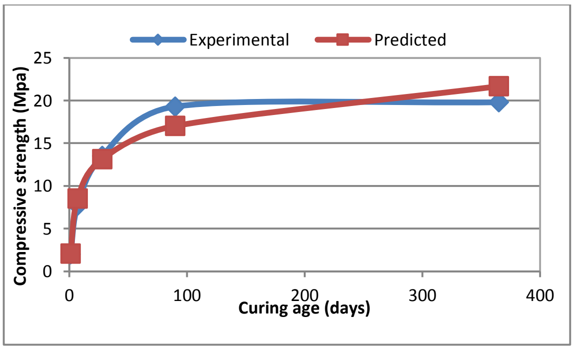
Figure ApxC.9: Experimental and predicted compressive strength for mortar mixes with different fly ash content and RSS/Binder ratios of 0.65 (Equation 8.3).



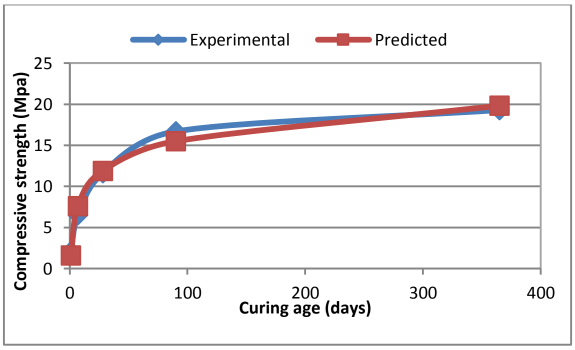
A: Fly ash content =0%



B: Fly ash content =10%

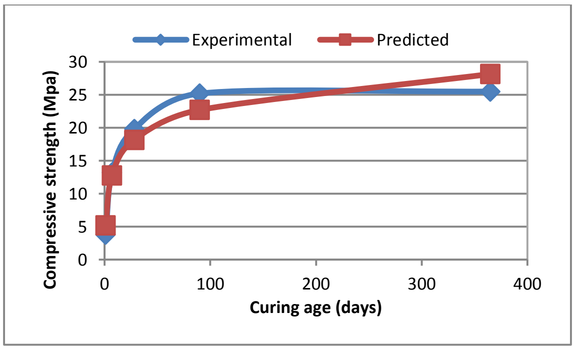


C: Fly ash content =20%

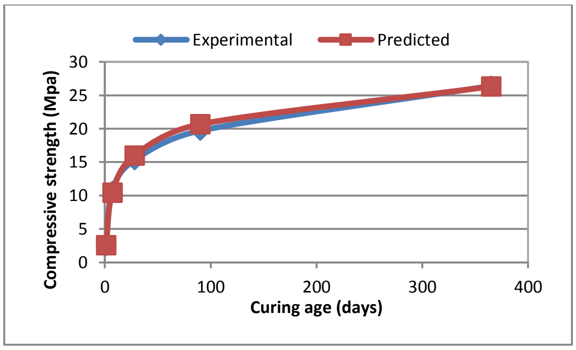


D: Fly ash content =30%

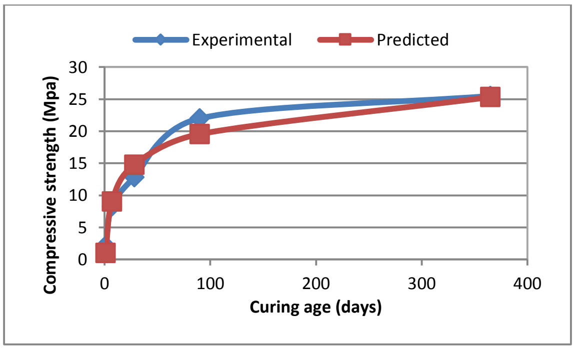
Figure ApxC.10: The relationship between the experimental and predicted compressive strength for mortar mixes with different fly ash content and RSS/Binder ratio of 0.8 (Equation 8.4).



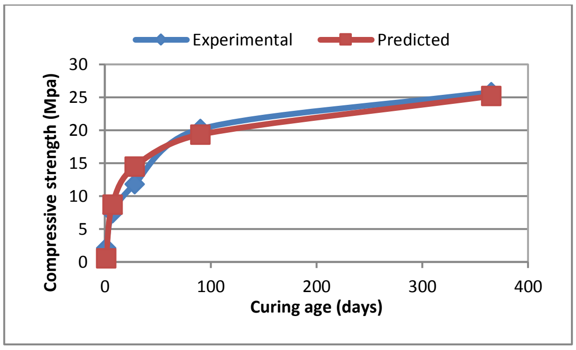
A: Fly ash content =0%



B: Fly ash content =10%

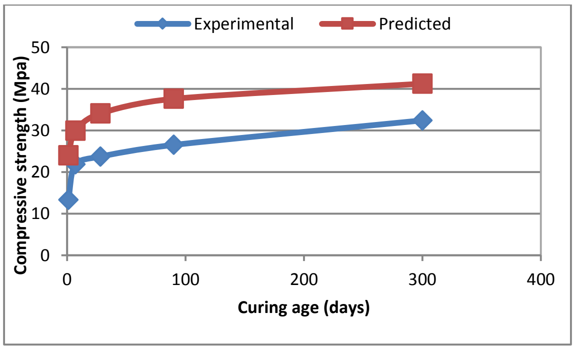


C: Fly ash content =20%

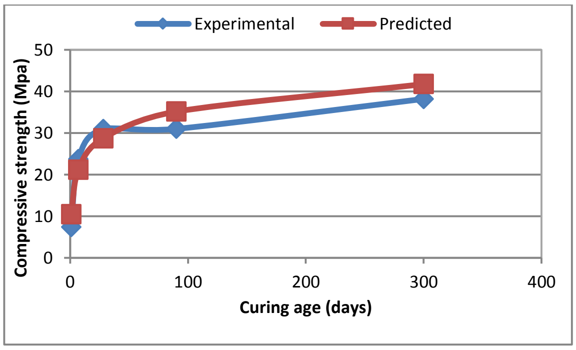


D: Fly ash content =30%

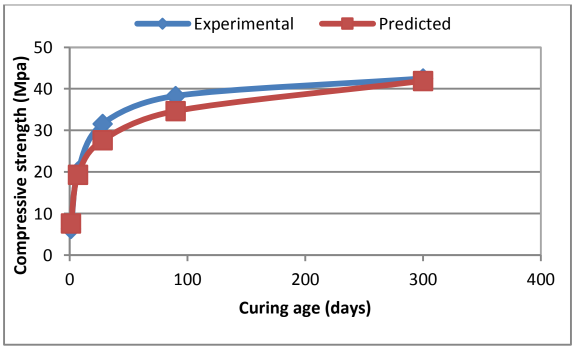
Figure ApxC.11: Experimental and predicted compressive strength for the control mixes with different fly ash content and Water/Binder ratio of 0.78 (Equation 8.5).



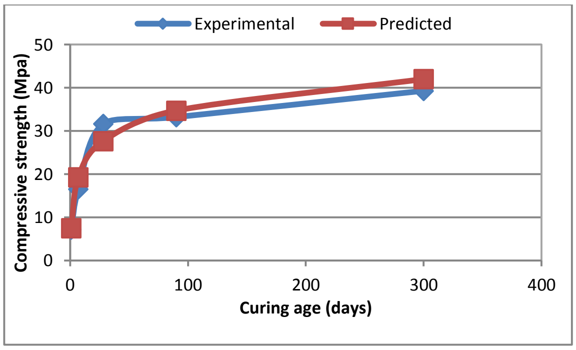
A: Fly ash content =0%



B: Fly ash content =10%



C: Fly ash content =15%



D: Fly ash content =20%

Figure ApxC.12: Actual and predicted compressive strength for concrete mixes with different fly ash content and RSS/Binder ratio of 0.5 (Equation 8.6).